ION PROBE MEASUREMENT OF OXYGEN SELF-DIFFUSION IN $\text{Al}_2\text{O}_3$

by

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ABSTRACT

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Submitted to the Department of Materials Science and Engineering on January 13, 1977 in partial fulfillment of the requirements for the degree of Doctor of Science.

Anion self-diffusion coefficients normal to (1102) have been obtained for single crystal Al2O3 in a 10⁻⁵ torr vacuum over a temperature range of 1584°C to 1839°C from concentration gradients measured by an ion probe. ¹⁸O tracer was supplied from an initial thin film produced by the oxidation of vapor-deposited Al metal films in ¹⁸O₂ gas at 520°C. Oxidation of Al metal results in a limiting thickness for the resulting oxide film so the Al films were deposited with 100Å thickness. In order to provide sufficient tracer to measure composition gradients over a penetration distance of 3,000Å to 5,000Å, the deposition-oxidation procedure was repeated 5 to 10 times. It was verified that mechanical damage done to the surface of single crystals of Al₂O₃ during polishing could be removed by annealing at 1600°C in air for four hours. Diffusion samples were prepared both from crystals that had been pre-annealed to remove surface damage and from as-polished crystals. The concentration profiles were measured with an ion probe using a static 10na to 30na primary ion beam of 5keV A⁺ ions focused to a uniformly-illuminated spot 100μm in diameter. The primary ion beam eroded the surface to produce a crater which exposed successively deeper depths to analysis. A correction procedure was developed to remove the component of the ion probe signal contributed by the sides of the crater. The diffusion coefficient was determined by fitting the thick-film solution of Fick's Second Law to the corrected data. The concentration profile of the as-polished samples did not fit the assumed solution but rather showed a broadening of the applied tracer film due to fast diffusion through the damaged surface layer. The concentration profiles of the pre-annealed sample fit the anticipated solution very well and yielded diffusion coefficients which may be described: $D=6.4(±31.0, -6.3)×10^5\exp(-188±7\text{kaal/mole/RT})\text{cm}^2/\text{sec}$. The result is interpreted as representing extrinsic diffusion.

Thesis Supervisor: Bernhardt J. Wuensch
Title: Professor of Ceramics
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I. INTRODUCTION

ALUMINUM OXIDE

Aluminum oxide or alumina is a ceramic material of considerable interest. It is used widely as a refractory and as an abrasive as well as in automobile spark plug insulators and as a substrate in electronic integrated circuits. It is also used in lasers and as an envelope in high intensity sodium vapor lamps. It is probably most commonly known as the gem stones sapphire and ruby. These are just a few of the applications of aluminum oxide.

Alumina has found so many uses because of its properties. It is a good electrical insulator. It has high strength and hardness, a high melting point and good resistance to chemical attack. An important step in understanding some of its properties is understanding how oxygen and aluminum diffuse within the solid. For example the electrical conductivity and creep are directly controlled by the movement of the oxygen and/or aluminum ions.

Alumina bodies are typically formed by sintering or hot pressing of aluminum oxide powder. The densification of these bodies depends on the rearrangement of the atoms and, in order to maintain local charge neutrality, will be limited by the slower moving species. To understand the fabrication process and improve on it, an understanding of the diffusion of the constituents is necessary.
DIFFUSION

While a solid can be thought of as a fixed array of atoms, it must be kept in mind that the atoms are not fixed but are vibrating about an equilibrium position. A vibrating atom can gain enough energy by interacting with its neighbors to break loose from its equilibrium position and move to a new location. This movement of atoms within a solid is called diffusion and the extent of this movement is called its diffusivity. This can be illustrated by considering a set of parallel planes separated by a distance $s$. Two adjacent planes termed Plane 1 and Plane 2 have respectively $n_1$ and $n_2$ atoms per unit area. If each atom jumps an average of $\Gamma$ times per second, the number of atoms leaving Plane 1 in a short time, $\Delta t$, will be $\Gamma n_1 \Delta t$. If the jumps are assumed to be at random, then one-half will be on to Plane 2. Likewise the number of atoms jumping from Plane 2 to Plane 1 in the time $\Delta t$, will be:

$$\frac{1}{2} \Gamma n_2 \Delta t$$

The net flow of particles from Plane 1 to Plane 2 will then be:

$$\Delta n = -\frac{1}{2} \Gamma (n_1 - n_2) \Delta t$$

Since $n_1$ and $n_2$ are surface concentrations, then $n_1/s = c_1$ and $n_2/s = c_2$ are the volume concentrations and the flux of particles per unit time is given by:

$$J = \frac{1}{2} (c_1 - c_2) s \Gamma$$
If \( a_2 = a_1 - s \frac{dc}{dx} \), then:

\[
J = -\frac{1}{2} s^2 \Gamma \frac{dc}{dx} = -D \frac{dc}{dx}
\]

Eq. 1.1

It is thus seen that the flux is proportional to the concentration gradient. The constant of proportionality is:

\[
D = \frac{1}{2} s^2 \Gamma
\]

where \( s \) is the jump distance and \( \Gamma \) is the jump frequency. \( D \) is called the diffusion coefficient or the diffusivity. It might be noted that if \( N \) jumps are made in time \( t \), then \( \Gamma = \frac{N}{t} \) and:

\[
Dt = \frac{1}{2} N s^2 = \frac{1}{2} \overline{x^2}
\]

Eq. 1.2

where \( \overline{x^2} \) is the mean square displacement of a particle after \( N \) random jumps of distance \( s \). The \( 1/2 \) in Equation 1.2 is the probability that the particle will jump in a given direction and applies only to the one dimensional case. In three dimensions the probability that a jump along any axis is the same so only one-third of the jumps will be along a given axis and:

\[
Dt = \frac{1}{6} \overline{x^2}
\]

In general:

\[
Dt = \gamma \overline{x^2} = \gamma s^2 \Gamma
\]

Eq. 1.3
where γ is a geometrical factor depending on the structure of the material. Thus it can be seen that the diffusivity need not necessarily be associated with a concentration gradient but is also an indication of the extent of the displacement of an atom moving randomly within a solid.

This random movement of the constituent atoms of a solid is called self-diffusion and has a self-diffusion coefficient defined by Equation 1.3. Since all atoms of a given species are identical, there is no way of directly establishing the displacement of a specific atom to obtain the self-diffusion coefficient. A useful diffusion coefficient can be measured using a small amount of a tracer atom. The resulting displacement gives the tracer diffusivity, $D^*$. If the tracer is an isotope of one of the constituents of the host crystal, then $D^*$ will approach the self-diffusivity, $D$, of that constituent. The differences between $D$ and $D^*$ will be discussed later in this chapter.

Since the kinetic energy of the atoms in a material increases with temperature, there will be more atoms moving and thus the diffusivity will increase with temperature. If the energy barrier to the movement of atoms is $\Delta G_m$, then using Boltzmann statistics, the probability than an atom has enough energy to surmount that barrier is given by:

$$P = \exp(-\Delta G_m/RT)$$

where $T$ is the absolute temperature and $R$ is the gas constant. The jump frequency can then be given by:
\[ \Gamma = \nu \exp(-\Delta G_m/RT) \]

where \( \nu \) is the frequency at which the atom is vibrating about its equilibrium position. The diffusivity can thus be given by:

\[ D = D_o \exp(-\Delta G_m/RT) \]  \hspace{1cm} Eq. 1.4

where:

\[ D_o = \gamma \nu \alpha^2 \exp(\Delta S_m/R) \]

**Mathematics of Diffusion**

Diffusion can be described mathematically by a set of phenomenological relationships proposed first by Adolph Fick in 1855. Fick's First Law which expresses the rate at which matter diffuses was derived in Equation 1.1. In three dimensions it is:

\[ \vec{J} = -D \nabla \alpha \]  \hspace{1cm} Eq. 1.5

Where \( \vec{J} \) is the flux of diffusing material, \( \alpha \) is the concentration of that material, \( D \) is the diffusion coefficient or diffusivity, and \( \nabla \) is the linear operator \( (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) \).

Fick's Second Law is derived from the first by recognizing that matter must be conserved. In one dimension it is stated as:
\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \tag{Eq. 1.6}
\]

where \( t \) is the time and the other parameters are the same as described above. If the diffusion coefficient does not vary with position then Equation 1.6 reduces to:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{Eq. 1.7}
\]

By applying the appropriate boundary conditions to Fick's Second Law the differential equation can be solved to give the concentration as function of position and time.

A thin film of tracer inserted in the center of an infinitely long bar provides the boundary conditions for one of the simplest solutions to Fick's Second Law. If the bar is heated so that the tracer will diffuse, the composition will be given by:

\[
c(x, t) = \frac{\alpha}{2\sqrt{\pi Dt}} \exp(-x^2 / 4Dt) \tag{Eq. 1.8}
\]

where \( c \) is the concentration of the tracer, \( x \) the distance from the original position of the tracer film, \( t \) the diffusion time, \( D \) the diffusivity and \( \alpha \) the total amount of tracer. This is called the "thin film solution" and it holds for a film thickness much less than \( \sqrt{Dt} \).
A solution for the case where the thickness of the tracer film is comparable to the extent of the diffusion can be obtained by dividing the film into a number of thinner films and superimposing the solutions. By taking the limit as the film is divided into thinner and thinner slices, the solution becomes:

\[ c = \frac{\alpha}{2\sqrt{\pi Dt}} \int_{-d}^{d} \exp\left\{-\frac{(x+y)^2}{4Dt}\right\} dy \]

Where \( y \) is the position of the thin film being considered. With the change of variable \( \eta = \frac{(x+y)/(2\sqrt{Dt})}{2\sqrt{Dt}} \), the solution becomes:

\[ c = \frac{c_0}{\sqrt{\pi}} \int_{x-d}^{x+d} \exp(-\eta^2) d\eta \quad \text{Eq. 1.9} \]

Where the thickness of the film is \( 2d \), \( c_0 \) is the initial concentration of tracer in the film and \( \eta \) is a dummy variable. This is the "thick film solution". If the error function is defined as:

\[ \text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} \exp(-\eta^2) d\eta \quad \text{Eq. 1.10} \]

the solution can be written:

\[ c(x,t) = \frac{c_0}{2} \left[ \text{erf}\left(\frac{d+x}{2\sqrt{Dt}}\right) + \text{erf}\left(\frac{d-x}{2\sqrt{Dt}}\right) \right] \quad \text{Eq. 1.11} \]
Since
\[ \frac{\partial c}{\partial x} \Big|_{x=0} = \frac{c_0}{2\sqrt{\pi Dt}} \left[ \exp\left(-\frac{(x+d)^2}{4Dt}\right) - \exp\left(-\frac{(x-d)^2}{4Dt}\right) \right] \Big|_{x=0} = 0 \]
and
\[ J = -D \frac{dc}{dx} \]
the flux at \( x=0 \) will always be zero indicating that there is no diffusion between the two halves so the solution for \( x<0 \) can be separated from that for \( x>0 \). Because of this, the thick film solution also holds for a semi-infinite bar with a tracer film of thickness \( d \).

The superposition of many thin film solutions is also used to solve the case where a semi-infinite bar with a tracer concentration of \( c_0 \) is joined to another semi-infinite bar with no tracer. By dividing the bar containing the tracer into segments and taking the limit as the thickness of the segments goes to zero, the result becomes:
\[ c(x,t) = \frac{c_0}{2\sqrt{\pi Dt}} \int_0^\infty \exp\left(-\frac{(x+y)^2}{4Dt}\right) dy \]
where \( y \) is the position of the film being considered. With the change in variable \( \eta = (x+y)/(2\sqrt{Dt}) \), the solution becomes:
\[ c(x,t) = \frac{c_0}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^\infty \exp(-\eta^2) d\eta \quad \text{Eq. 1.12} \]
Using the definition of the error function the solution becomes:

$$c(x,t) = \frac{c_0}{2} \{1 + \text{erf}(x/2\sqrt{Dt})\}$$  \hspace{1cm} \text{Eq. 1.13}

Since $c(0,t) = c_0/2$ for all $t$, this solution can also be used in the case where the concentration at a surface of a semi-infinite solid is a constant. These are a few of the more useful solutions.

**Diffusion Mechanisms**

While Fick's Laws are useful in describing the effects of diffusion, they give no clue to the mechanism by which it takes place. In a crystalline solid there are a number of mechanisms by which diffusion can take place. It has been proposed that atoms can move by a direct exchange of position. However, the large strain energy needed to squeeze two atoms past each other makes that mechanism improbable. A ring mechanism in which a closed circle of three or more atoms can rotate, may be possible though it has not been clearly demonstrated experimentally.

A mechanism that has been observed and is considered important is diffusion by atoms on interstitial sites. Diffusion by this mechanism requires the presence of interstitial atoms. The number of interstitials is limited by the energy required for their formation. This includes the energy associated with the distortion of the lattice caused by an interstitial and the Coulomb energy due to its charge. There is also an energy barrier associated with the lattice distortion during the movement of an interstitial atom to a new interstitial site. The interstitialcy mechanism is a variation of interstitial diffusion in which an
interstitial atom moves to an occupied normal site, knocking that atom into another interstitial site. This mechanism can occur when the direct movement between interstitial sites is improbable.

Possibly the most common mechanism is that by vacancies, since vacancies, in thermodynamic equilibrium or created by aliovalent impurities, are present in all crystalline solids. Diffusion by the vacancy mechanism involves the movement of an atom from a normal site to a vacant adjacent site. The energy barrier for this motion includes that required to distort the lattice as the atom moves to the vacant site, the Coulomb energy due to its charge plus other terms. In this case it is convenient to talk about the diffusion of the vacancy and its diffusivity.

In cases where diffusion is by a defect mechanism, the tracer diffusivity is related to that of the pertinent defect, \( D^d \), by:

\[
D^* = f \sigma_d D^d
\]

Eq. 1.14

where \( f \) is a correlation factor and \( \sigma_d \) is the molar fraction of the defect. The correlation factor is less than 1 for the vacancy and interstitialcy mechanisms but is equal to 1 for the interstitial mechanism. This factor is required to account for the correlation of an atomic jump with previous jumps. In the vacancy mechanism, the correlation effect can be illustrated by considering a tracer ion that has just jumped on to a vacant site leaving a vacancy behind. It can be seen that with this initial configuration, the probability that the tracer will make its next jump back on to its former site is greater than the probability that it will jump onto one of the other neighbor-
ing sites which are initially occupied. Similar reasoning applies for the interstitialcy mechanism. Thus, $f$ for the vacancy and interstitialcy mechanisms is less than 1. Since the probability of a tracer ion jumping back into the site it had just vacated decreases as the number of ions that can jump into it increases, the correlation factor is a function of the crystal structure. For the interstitial mechanism where the concentration of interstitials are low enough so that each interstitial is surrounded by empty interstitial sites, then its jumps will be independent and $f=1$. Since the self-diffusivity is related only to the number of jumps of any atom, the self-diffusion coefficient is related to the defect diffusivity by:

$$D = c_d D^d$$

Eq. 1.15

and

$$D^* = fD$$

Eq. 1.16

Other mechanisms have also been proposed but interstitial and vacancy diffusion are considered to be by far the most important.

**Defect Structure**

Since diffusion by a defect mechanism depends on the concentration of the appropriate point defect, it is important to understand the formation of these defects. In ionic compounds such as ceramics, the point defects have an effective charge and the concentration of vacancies and interstitials must be related in order to maintain charge neutrality. Because of the need to maintain local charge neutrality, at least two
types of oppositely charged defects must be formed. Two such arrangements are called the "Schottky disorder" and the "Frenkel disorder".

In the "Schottky disorder" there are an appropriate number of negatively charged cation vacancies for each positively charged anion vacancy to maintain charge neutrality. In the "Frenkel disorder", there is an interstitial formed for each oppositely charged vacancy. As an example, the defect reactions in Al$_2$O$_3$ can be written using the notation developed by Kroger and Vink$^2$:

\[
\text{Schottky null} = 2V_{\text{Al}^{''''}} + 3V_{\text{O}^{...}} \quad K_S \quad \text{Eq. 1.17}
\]

\[
\text{Frenkel} \quad A_{\text{Al}}^{...} = V_{\text{Al}^{''''}} + A_{\text{i}}^{...} \quad K_f \quad \text{Eq. 1.18}
\]

$V_{\text{Al}^{''''}}$ represents a vacant aluminum site, $V_{\text{O}^{...}}$ a vacant oxygen site, $A_{\text{i}}^{...}$ an aluminum interstitial and $A_{\text{Al}}^{...}$ an aluminum on an aluminum site. A (') represents a negative effective charge and a (') represents a positive effective charge. $K_S$ and $K_f$ are the equilibrium constants for the two reactions and are given by:

\[
K_S = [V_{\text{Al}^{''''}}]^2[V_{\text{O}^{...}}]^3 = \exp(-\Delta G_S/RT) \quad \text{Eq. 1.19}
\]

\[
K_f = [V_{\text{Al}^{''''}}][A_{\text{i}}^{...}] = \exp(-\Delta G_f/RT) \quad \text{Eq. 1.20}
\]

where the brackets signify concentrations. A Frenkel disorder reaction can also be written for the oxygen ions. However, since the oxygen ions form a hexagonal close packed array, the energy associated with an oxygen interstitial would be quite large. It is therefore unlikely to be important. In order to maintain charge neutrality:
By solving the three equations 1.19, 1.20, and 1.21, the defects concentrations can be found. The native concentration of aluminum vacancies is:

\[
[V_{Al}'''] = \{1 + \frac{2}{3} \exp\{- (\Delta G_e / 3 - \Delta G_f ) / RT \} [V_{Al}''']\}^{\frac{2}{3}} \exp\{- \Delta G_f / RT \} \quad \text{Eq. 1.22}
\]

If \( \Delta G_e / 5 \gg \Delta G_f / 2 \) then:

\[
[V_{Al}'''] = \exp\{- \Delta G_f / 2RT \}
\]

\[ [Al_i''''] = \exp\{- \Delta G_f / 2RT \} \quad \text{Eq. 1.23} \]

\[ [V_0'''] = \exp\{- (\Delta G_e - \Delta G_f) / 3RT \} \]

If \( \Delta G_f / 2 \gg \Delta G_e / 5 \) then:

\[
[V_{Al}'''] = (2/3)^{\frac{3}{2}} \exp\{- \Delta G_e / 5RT \}
\]

\[ [Al_i''''] = (3/2)^{\frac{3}{2}} \exp\{- (\Delta G_f - \Delta G_e / 5) / RT \} \quad \text{Eq. 1.24} \]

\[ [V_0'''] = (3/2)^{\frac{3}{2}} \exp\{- \Delta G_e / 5RT \} \]

These are called native or intrinsic defects.

The defect concentration can be affected by any aliovalent impurities present. This can be demonstrated by continuing with the example of \( \mathrm{Al}_2\mathrm{O}_3 \). If a cation impurity having a +2 valence such as Mg is added, then a possible reaction would be:
\[ 3\text{MgO} + \text{Al}_{\text{Al}}^x = 3\text{MgAl}^\prime + \text{Al}_{\text{i}}\cdots + 3\text{O}_0 \quad \text{Eq. 1.25} \]

For temperatures low enough that the native aluminum interstitial concentration is much less than that created by the dissolution of MgO then the interstitial concentration will be fixed by the impurity concentration and:

\[ [\text{Al}_{\text{i}}\cdots] = \frac{1}{3} [\text{MgAl}^\prime] \quad \text{Eq. 1.26} \]

Solution of equations 1.19, 1.20, and 1.26 gives:

\[ [V_{\text{Al}'''}] = \frac{3}{[\text{MgAl}^\prime]} \exp(-\Delta G_f/RT) \]
\[ [V_{O\cdots}] = \left(\frac{1}{3} [\text{MgAl}^\prime]\right)^2 \exp\{-\frac{1}{3} (\Delta G_f - 2\Delta G_f/RT)\} \quad \text{Eq. 1.27} \]

If a cation impurity having a +4 valence such as Si is added then a possible dissolution reaction would be:

\[ 3\text{SiO}_2 = 3\text{Si}_{\text{Al}}^\prime + V_{\text{Al}'''} + 6\text{O}_0 \quad \text{Eq. 1.28} \]

For temperatures low enough that the native aluminum vacancy concentration is much less than that created by the dissolution of the SiO\(_2\), then the vacancy concentration will be fixed by the impurity concentration and:

\[ [V_{\text{Al}'''}] = \frac{1}{3} [\text{Si}_{\text{Al}}^\prime] \quad \text{Eq. 1.29} \]
Solution of equations 1.19, 1.20 and 1.29 gives:

\[
\left[ \text{Al}_{\text{\ldots}} \right] = \frac{3}{[\text{SiAl}_{\text{\ldots}}]} \exp(-\Delta G_f/RT) \\
\text{and} \\
\left[ \text{V}_0 \right] = \left( \frac{3}{[\text{SiAl}_{\text{\ldots}}]} \right)^{\frac{3}{2}} \exp(-\Delta G_s/3RT)
\]

Eq. 1.30

Those defects whose concentrations are controlled by the impurity concentration are called extrinsic.

For the above defect reactions it is assumed that the defects are randomly distributed throughout the material and that they form an ideal solution. Defect complexes are also possible in which the defects form clusters instead of being distributed randomly. Since the defects are charged, there is a Coulomb attraction between oppositely charged defects that can bind them together. For example, a vacancy or interstitial might be bound to an impurity, a vacancy bound to an interstitial, or a cluster of anion and cation vacancies could be bound together. Other defects could also be formed such as vacancies or interstitials with different effective charges. In considering possible defect reactions, three conditions must be maintained: (1) mass must be conserved; (2) charge neutrality must be maintained; and (3) the ratio of cation to anion sites must be kept constant.

Since tracer diffusivity is related to the defect concentration by:

\[
D^* = f_o D^d \\
D^d = D^d_0 \exp(-\Delta H_m/RT)
\]
then:

\[ D^* = f e \frac{D_o D e}{D_o} \exp\left(-\frac{\Delta H_m}{RT}\right) \]

By noting that:

\[ \Delta G = \Delta H - T\Delta S \]

Then:

\[ \exp(-\Delta G/RT) = \exp(-\Delta H/RT + \Delta S/R) = K_0 \exp(-\Delta H/RT). \]

Using the defect concentrations calculated for Al₂O₃, the tracer diffusivities can be written:

**Intrinsic**

**Frenkel Dominant**

Vacancy \[ D^A_L = f^{\nu_a} K_f^{\nu_o} D_o^{\nu_o} e^{-\left(\frac{\Delta H_f}{2} + \frac{\Delta H_m^{\nu_o}}{2}\right)/RT} \]

Interstitial \[ D^I_L = f^{\nu} (K_f^{\nu})^{\frac{1}{2}} D_o^{\nu} e^{-\left(\frac{\Delta H_f}{2} + \frac{\Delta H_m^{\nu}}{2}\right)/RT} \]

**Vacancy** \[ D^0 = f^{\nu_o} (K_f^{\nu_o} / K_f^{\nu_o})^{\frac{1}{2}} D_o^{\nu_o} e^{-\left[\frac{\Delta H_s - \Delta H_f}{3} + \Delta H_m^{\nu_o}\right]/RT} \]

**Schottky Dominant**

Vacancy \[ D^A_L = f^{\nu_a} (8 K_f^{\nu_o} / 27)^{\frac{1}{2}} D_o^{\nu_o} e^{-\left(\frac{\Delta H_s}{5} + \frac{\Delta H_m^{\nu_o}}{5}\right)/RT} \]

Vacancy \[ D^0 = f^{\nu_o} (9 K_f^{\nu_o} / 4)^{\frac{1}{2}} D_o^{\nu_o} e^{-\left(\frac{\Delta H_s}{5} + \Delta H_m^{\nu_o}\right)/RT} \]

**Extrinsic - Frenkel Dominant (within the solubility limit)**

**MgO Doped**

Vacancy \[ D^A_L = f^{\nu_a} (3 K_f^{\nu_o} / 4)^{\frac{1}{2}} D_o^{\nu_o} e^{-\left(\frac{\Delta H_s}{5} + \frac{\Delta H_m^{\nu_o}}{5}\right)/RT} \]
Interstitial $D^{Al}_i = f^i [Mg] D^{i} e^{-\Delta H^i_m / RT}$

Vacancy $D^O_v = f^v [Mg] (\frac{[Mg]}{3k^f_O})^2 D^v e^{-[\frac{(\Delta H^g_s - 2\Delta H^f_f) / 3 + \Delta H^v_m}{RT}]}$

**SiO$_2$ Doped**

Vacancy $D^{Al}_v = f^v [Si] D^v e^{-\Delta H^v_m / RT}$

Interstitial $D^{Al}_i = f^i 3k^f_O D^i e^{-(\Delta H^s_f + \Delta H^i_f) / RT}$

Vacancy $D^O_v = f^v [Si] (\frac{3}{[Si]})^2 K^a_O D^v e^{-(\Delta H^s / 3 + \Delta H^v_m^v) / RT}$

The superscripts refer to the pertinent ion or defect. For the defects $va$ signifies an aluminum vacancy, $vo$ an oxygen vacancy, and $i$ and aluminum interstitial. The constants $K^a_O$, $K^f_O$ represent the entropies of formation for the Schottky and Frenkel defect arrays.

**Diffusion Controlled Processes**

 Ionic electrical conductivity in ceramics is a result of diffusion of a charged ion or defect. Electrical conductivity can also occur by the movement of electrons or holes. The total conductivity is given by:

$$\sigma = \sigma_{el} + \sigma_{ionic} = \sigma (t_e + t_i)$$  \hspace{1cm} Eq. 1.34

where $t_e$ and $t_i$ are called the transference numbers for electrical and ionic conductivity and represent the fraction of the conductivity provided by each. The electric current density due to ionic diffusion is given by:
\[ j_i = \sigma_i z_i e v_i \]

\( \sigma_i \) is the concentration of the diffusing species, \( z_i e \) its effective charge, and \( v_i \) its drift velocity. The velocity is related to the applied electric field, \( \xi \), by:

\[ v_i = z_i e B_i \xi \]

where \( B_i \) is called the mobility. But since \( j_i = \sigma_i \xi \):

\[ \sigma_i = \sigma_i z_i^2 e^2 B_i \]  \hspace{1cm} \text{Eq. 1.35} \]

The ionic conductivity \( \sigma_i \) is related to the diffusivity by the Nernst-Einstein Equation:\(^3\,^4\)

\[ D_i = B_i kT \]  \hspace{1cm} \text{Eq. 1.36} \]

Thus:

\[ \sigma_i = \frac{\sigma_i z_i^2 e^2}{kT} D_i \]  \hspace{1cm} \text{Eq. 1.37} \]

Ionic conductivity is dominated by the fastest diffusing species.

Diffusional creep is a deformation process that takes place by the diffusion of material along a chemical potential gradient resulting from an applied stress. The chemical potential gradient occurs because of the variation in the normal boundary stress produced by the applied
stress. Since charge neutrality must be maintained, the creep rate will be controlled by the slower moving species. For creep controlled by lattice diffusion, commonly called Nabarro-Herring creep, the strain rate is given by:

$$\dot{\epsilon} = \frac{(18.3D_l\Omega \sigma)}{kT(GS)^2}$$  \hspace{1cm} \text{Eq. 1.38}

where $D_l$ is the lattice diffusion coefficient, $\Omega$ the molecular volume, $\sigma$ the applied stress and $GS$ the grain size. For creep that is controlled by diffusion in the grain boundaries, commonly called Coble creep, the strain rate is given by:

$$\dot{\epsilon} = \frac{[47\Omega_D(\delta D_b)\sigma]}{kT(GS)^3}$$  \hspace{1cm} \text{Eq. 1.39}

where $\delta D_b$ is the product of the effective grain boundary width and the grain boundary diffusivity.

Sintering is the term used to describe the process by which a low density powder compact consolidates into a dense polycrystalline solid at elevated temperatures. Hot pressing, often called pressure sintering, is a similar process in which pressure is applied to the compact during heating. The consolidation and densification is the result of various mechanisms depending on, among other things, the material and the temperature. While surface diffusion and evaporation and condensation can strengthen the powder compact, they cannot densify it. Grain boundary diffusion or lattice diffusion are the only diffusional mechanisms that
can cause densification of the compact. Like creep, sintering is controlled by the slower diffusing species. There have been many models proposed for the sintering process, but no one model can describe the whole process. Sintering has typically been divided into three stages: an initial stage, an intermediate stage, and a final stage with a separate model for each stage. The shrinkage of the compact during the initial stage for both sintering and hot pressing controlled by lattice diffusion as predicted by Coble's model is:

\[ 16(\frac{\Delta L}{L_0})^2 = \frac{32D_L\Omega}{R^4kT}[\gamma+(P_aR/\pi)]t \quad \text{Eq. 1.40} \]

\( (\Delta L/L_0) \) is the linear shrinkage or the compact, \( D_L \) the lattice diffusivity of the rate controlling species, \( \Omega \) the vacancy volume, \( R \) the radius of the particles, \( \gamma \) the surface energy and \( t \) the time. In the case of hot pressing \( P_a \) is the applied pressure. A similar expression for the case where boundary diffusion is rate controlling is:

\[ 64(\frac{\Delta L}{L_0})^3 = \frac{96\delta D_b\Omega}{R^4kT}[\gamma+(P_aR/\pi)]t \quad \text{Eq. 1.41} \]

\( D_b\delta \) is the product of the boundary diffusivity and the effective boundary width. Models for the intermediate and final stages have been developed, based on the creep models already mentioned. The driving force for densification is \((P_a/\rho + \gamma/r)\) for the intermediate stage, and \((P_a/\rho + 2\gamma/r)\) for the final stage. Here \( r \) is the radius of the pores and \( \rho \) is the density of the material.
MEASURING DIFFUSION

A common technique used in measuring diffusion employs a radioactive isotope as a tracer. The tracer is deposited on the desired sample in a fashion which provides one of the boundary conditions that produce a simple solution to Fick's Second Law. Typically, it is applied as a thin film in order to limit the amount of expensive and potentially hazardous isotope material. After annealing the sample for the desired time, thin sections of known thickness are successively ground from the surface. Since the concentration of tracer is proportional to the specific activity in a section, the concentration profile is established by measuring the radioactivity of each section. The diffusion coefficient is then extracted from the concentration profile. This technique is suitable for both self-diffusion and impurity diffusion studies. Unfortunately, many chemical species (including oxygen and aluminum) do not have suitable radioactive isotopes. The radioactive isotopes of aluminum and oxygen are shown in Table 1.1. The half life of the radioactive isotopes of oxygen are all too short for experiments which may require many days to complete. Most of the radioactive isotopes of aluminum also have a half life that is too short. However, one has a half life that is too long to provide activities of a useful level. While the short half life isotopes will vanish before the experiment is finished, the specific activity of the long half life isotope is too small to measure accurately.

For measuring the diffusion of a species which is chemically different from the host material, common chemical analysis techniques are suitable. The electron microprobe as well as Auger spectroscopy
### Table 1.1
Isotopes

#### OXYGEN ISOTOPES

<table>
<thead>
<tr>
<th>Mass</th>
<th>% Natural Abundance</th>
<th>Half Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>*</td>
<td>0.0037 sec.</td>
</tr>
<tr>
<td>14</td>
<td>*</td>
<td>76.5 sec.</td>
</tr>
<tr>
<td>15</td>
<td>*</td>
<td>124 sec.</td>
</tr>
<tr>
<td>16</td>
<td>99.76</td>
<td>stable</td>
</tr>
<tr>
<td>17</td>
<td>0.04</td>
<td>stable</td>
</tr>
<tr>
<td>18</td>
<td>0.20</td>
<td>stable</td>
</tr>
<tr>
<td>19</td>
<td>*</td>
<td>29 sec.</td>
</tr>
<tr>
<td>20</td>
<td>*</td>
<td>14 sec.</td>
</tr>
</tbody>
</table>

#### ALUMINUM ISOTOPES

<table>
<thead>
<tr>
<th>Mass</th>
<th>% Natural Abundance</th>
<th>Half Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>*</td>
<td>2.1 sec.</td>
</tr>
<tr>
<td>25</td>
<td>*</td>
<td>7.2 sec.</td>
</tr>
<tr>
<td>26M</td>
<td>*</td>
<td>6.4 sec.</td>
</tr>
<tr>
<td>26</td>
<td>*</td>
<td>7.4x10^5 yrs.</td>
</tr>
<tr>
<td>27</td>
<td>100</td>
<td>stable</td>
</tr>
<tr>
<td>28</td>
<td>*</td>
<td>2.31 min.</td>
</tr>
<tr>
<td>29</td>
<td>*</td>
<td>6.6 min</td>
</tr>
<tr>
<td>30</td>
<td>*</td>
<td>3.3 sec.</td>
</tr>
</tbody>
</table>
have been used quite successfully for these types of studies. Chemical techniques are not, by themselves, suited for measuring self-diffusion.

A number of techniques have been developed using a stable isotope tracer to measure self-diffusion. A gas-exchange technique has been used in which a sample is annealed in a closed system which contains a gas of the isotopic tracer. By monitoring the composition of the gas during the anneal, the dissolution of the tracer can be measured from which the diffusivity can be extracted.\(^9\)

Nuclear activation has been used to transform a stable isotope tracer into a radioactive species. For example \(^{18}\)O can be transformed into \(^{18}\)F which is radioactive by bombardment with a proton of the proper energy, while \(^{16}\)O is unaffected. After the \(^{18}\)O atoms have been activated in a cyclotron, the \(^{18}\)O diffusivity can then be measured using the sectioning techniques used with radioactive tracers.\(^{10}\) \(^{18}\)O can also be transformed into \(^{15}\)N by reaction with protons of a different energy. In this reaction an alpha particle is emitted. The alpha particle collides with atoms in the solid during emission. This causes a loss in energy and those originating deep in the sample will have lower energy on leaving the sample than those produced near the surface. The concentration profile of the \(^{18}\)O can thus be derived from the energy distribution of the alpha particles.\(^{11}\)

These techniques do not measure self-diffusion. What is measured is the tracer diffusion of one isotope in a solid composed primarily of another isotope. While the two isotopes are essentially the same chemically, they do have a different mass. As indicated in Equation
1.3, the diffusivity is proportional to a jump frequency $\Gamma$. In the case where the jump motion is assumed independent of the surrounding atoms, the ratio of the jump frequencies of the two isotopes may be approximated by the simple relationship:

$$\frac{\Gamma^*}{\Gamma} = (\frac{M}{M^*})^{\frac{1}{2}}$$

Eq. 1.42

which then gives:

$$D^* = (\frac{M}{M^*})^{\frac{1}{2}} D$$

Eq. 1.43

Since ionic electrical conductivity, sintering and creep are controlled by diffusion, such data have also been used to calculate self-diffusivities. Even though the ionic conductivity is dominated by the faster moving species, it may not always be clear which species that is. Nor is it always clear whether the electrical conductivity is electronic or ionic. Sintering and creep are both controlled by the slower moving species, but it is not always clear which species is the slowest. The effects of grain boundary diffusion are also hard to extract.

The development of the ion probe or secondary ion mass spectrometer (SIMS) offers a potentially simple technique to measure self-diffusion using a stable isotope tracer, but one which has not, as yet, been extensively explored.

Some techniques for measuring diffusion in general, including interdiffusion and self-diffusion, have been mentioned. A more detailed discussion on self-diffusion in $\text{Al}_2\text{O}_3$ including specific experiments
is contained in the Survey of Related Work.

ION PROBE

The ion probe or secondary ion mass spectrometer uses a beam of ions to sputter material from the surface of a sample. The secondary ions are, in turn, accelerated into a mass spectrometer to be analyzed. If the primary beam is focused to a fine point, the ion probe may be used in a way analogous to the use of an electron microprobe. Surface composition at a point may be analyzed in this way. Since material is sputtered from the surface by the primary beam, the ion probe can also be used to analyze the composition of the sample as a function of depth. By rastering the finely-focused beam over a small area or by defocusing the beam, a flat-bottomed crater may be produced. By relating the spectrometer analysis as a function of time to the crater depth as a function of time, the composition can be obtained as a function of depth.

As a tool for chemical analysis the ion probe is best suited for qualitative analysis. Because the ionization of the secondary particles vary from species to species and also are a function of the composition, quantitative analysis is more difficult. A few models have been developed with moderate success to predict the ionization yield and thus allow the ion probe to be directly used for quantitative analysis. Of course standards could be prepared to provide the output levels for known concentrations of constituents.

The ion probe is particularly suited for studies that involve the relative abundance of isotopes of the same chemical specie. Isotopes
are essentially identical chemically and therefore their ionization yields should be the same. The ion probe is therefore ideal for self-diffusion studies which use a stable isotope as a tracer.
SURVEY OF RELATED WORK

SELF-DIFFUSION IN $\text{Al}_2\text{O}_3$

As already indicated, diffusion in solids involves the movement of point defects. An understanding of self-diffusion in $\text{Al}_2\text{O}_3$ thus requires a knowledge of the defect structure. Both a knowledge of the number of defects and their mobility is required.

The structure of $\text{Al}_2\text{O}_3$ is based upon a hexagonal close-packed array of oxygen ions. The aluminum ions occupy $2/3$ of the octahedral interstices. Since the oxygens form a close-packed array, it seems unlikely that many oxygen interstitials will be formed. On the other hand, since the aluminum ions only fill $2/3$ of the octahedral interstices, it seems quite probable that aluminum interstitials will be formed.

Work that has been done to measure directly self-diffusion in $\text{Al}_2\text{O}_3$ will be surveyed. Studies of the diffusion-controlled processes, ionic conductivity, creep and sintering will also be surveyed. The results of these studies will be analyzed to establish their significance in understanding the diffusion mechanism and the defect structure.

Aluminum

Paladino and Kingery $^{14}$ measured aluminum self-diffusion in polycrystalline aluminum oxide using a radioactive isotope tracer. The $^{26}\text{Al}$ tracer is a cyclotron product available only with low specific
activity (3x10^4 disintegrations/min/gm). The low specific activity is a result not only of the long half life of the isotope, but also of the low enrichments available (less than 1,000ppm). The "thin film" boundary conditions therefore could not be used. In order to have sufficient tracer present to measure the specific activity, semi-infinite source diffusion couples were prepared. Because of the low specific activity, the diffusivity was calculated from the total amount of tracer that crossed the interface. The composition was determined at a few depths to be compared with that predicted by their measured diffusivity. Polycrystalline diffusion couples were prepared by hot pressing $^{26}$Al enriched aluminum oxide powder against polycrystalline disks with a grain size of 130μm. The grain size of the tracer enriched layer was 200μm after pressing. The impurities in the samples were reported to be Mg, Ca, Fe, Mn, and Si with less than 100ppm each. All attempts to hot press the tracer enriched powder to a single crystal failed because the samples shattered on cooling. Their result for the polycrystalline material was:

$$D = 28 \exp(-114\pm15\text{ kcal/mole/RT}) \text{cm}^2/\text{sec}$$

between 1670°C and 1905°C. They supposed this was intrinsic lattice diffusion.

While they concluded that the diffusivity measured was intrinsic, the stated impurity levels seem too high to support that conclusion. They also concluded that since the shape of the composition profile
fit that predicted by the calculated diffusivity, the process was lattice diffusion. The low specific activity of the tracer does leave some uncertainty about their results.

Oxygen

Oishi and Kingery\textsuperscript{9} measured oxygen self-diffusion using a gas-exchange technique. They used three types of samples: .03 in. single crystal spheres, 200-230 mesh grains obtained by crushing single crystal rods and 60-65 mesh polycrystalline grains obtained by crushing sintered wafers having a grain size of 20μm to 30μm. In most cases the samples were annealed in $^{18}$O\textsubscript{2} enriched oxygen at 1 atm for a specified time. The diffusivity was calculated from the total amount of $^{18}$O present in the samples. The samples were analyzed for $^{18}$O by reducing the Al\textsubscript{2}O\textsubscript{3} in graphite to obtain CO. The CO was converted to CO\textsubscript{2} by catalytic decomposition on red-hot iron and the CO\textsubscript{2} was analyzed in a mass spectrometer to obtain the $^{18}$O/$^{16}$O ratio. In order to make sure that the measured diffusivities were not a function of annealing time, the composition of the gas surrounding the samples was monitored during some of the annealing runs. If the process taking place were controlled by a single diffusion mechanism, then the diffusivity calculated from the amount of $^{18}$O dissolved in the solid (in other words, removed from the gas) at any particular time would be a constant. If the calculated diffusivity were a function of time, this would indicate that another process was rate controlling or at least that a competing mechanism was present. For the single crystal samples, this was done at 1715°C and 1753°C with the result that the diffusivities did not
vary with time. With the polycrystalline samples, the effective diffusivity decreased as time progressed, suggesting that the oxygen-uptake was not controlled by a single process.

For single crystals between 1650°C and 1780°C, their results were:

\[
D = 1.9 \times 10^3 \exp(-152 \pm 25 \text{ kcal/mole/RT}) \text{ cm}^2/\text{sec}
\]

Below 1650°C, there were large discrepancies between samples. Those that had been annealed at 1900°C prior to the exchange anneal, as well as some other samples, could be described by extrapolation of the high temperature diffusivities. Some other samples, however, showed diffusivities substantially higher which were given by:

\[
D = 1.9 \times 10^{-8} \exp(-57.6 \text{ kcal/mole/RT}) \text{ cm}^2/\text{sec}
\]

They concluded the high temperature diffusivity represents intrinsic behavior and that with the lower activation energy represents extrinsic behavior. For the polycrystalline samples the diffusion coefficient was found to be:

\[
D = 2.0 \exp(-110 \pm 15 \text{ kcal/mole/RT}) \text{ cm}^2/\text{sec}
\]

They attribute the higher diffusivity in polycrystalline material to enhanced diffusion at grain boundaries. The decrease in diffusivity that they observed with time was attributed to lattice diffusion from the boundaries into the grains.
It should be noticed that the two temperatures at which the gas composition was monitored to determine if the diffusivity were independent of time were well above the temperature where discrepancies between the samples were seen. Because of the large discrepancies among samples at the lower temperatures, it seems that there is not enough information available to interpret these data. The impurity levels stated seem too large to have intrinsic diffusion at such a low temperature.

Anderson\textsuperscript{10} measured oxygen self-diffusivity in single crystal Al\textsubscript{2}O\textsubscript{3} by using a nuclear activation technique to measure the abundance of an \textsuperscript{18}O tracer. He prepared samples by the deposition and oxidation in \textsuperscript{18}O\textsubscript{2} gas of aluminum metal on an Al\textsubscript{2}O\textsubscript{3} substrate. He applied about a 300\AA Al\textsubscript{2}O\textsubscript{3} film by the successive deposition and oxidation of 100\AA aluminum films. The samples were annealed in a flowing nitrogen atmosphere. Following the diffusion anneal these samples were placed in a cyclotron where they were bombarded by protons with a kinetic energy of 2.7 MeV. Under these conditions, the \textsuperscript{18}O transforms to \textsuperscript{18}F which is radioactive with a half-life of 110 minutes. The concentration profile of the \textsuperscript{18}F was measured by grinding off sections and measuring the radioactivity of each section. Determination of the original \textsuperscript{18}O concentration profile from the \textsuperscript{18}F profile presents the greatest limitation to this technique. The probability of an \textsuperscript{18}O ion being activated is a complex function of its depth in the sample. This arises from the proton energy being attenuated as it penetrated the sample and from the non-linear energy dependence of the cross-section
for the activation reaction. His results for a temperature range of 1650°C to 1900°C were:

\[ D = 3.0 \exp\left(-\frac{128 \text{ kcal/mole/RT}}{R T}\right) \text{cm}^2/\text{sec} \]

for Czochralski-grown single crystals and:

\[ D = 15.3 \exp\left(-\frac{126 \text{ kcal/mole/RT}}{R T}\right) \text{cm}^2/\text{sec} \]

for Verneuil-grown crystals. The verneuil crystals had a dislocation density of 7.4x10^4/cm³ while the Czochralski-grown crystals had a density of only 6.3x10^3/cm². The higher diffusivity in the Verneuil crystals was thus attributed to dislocation-enhanced diffusion. From the two diffusivities and the dislocation densities, Anderson calculated a lattice diffusivity of:

\[ D = 1.6 \exp\left(-\frac{128 \text{ kcal/mole/RT}}{R T}\right) \text{cm}^2/\text{sec} \]

By assuming an effective dislocation radius of 300Å, he calculated the dislocation pipe diffusion to be:

\[ D = 8.5 \times 10^6 \exp\left(-\frac{128 \text{ kcal/mole/RT}}{R T}\right) \text{cm}^2/\text{sec} \]

It was subsequently found that he miscalculated the thickness of the sections. From the weight of the material reported in each section
and the density of $\text{Al}_2\text{O}_3$, the actual thickness of the sections were ten times the reported thickness. The concentrations at these penetrations are much too large for the amount of tracer initially applied. The observed results cannot therefore be attributed to the diffusion of oxygen but perhaps could be related to the activation of the naturally occurring $^{18}_0$ in the samples by the incident protons as they penetrated the solid.

Reddy and Cooper$^{11}$ also used a nuclear activation technique to measure the concentration profile of an $^{18}_0$ tracer. They bombarded their samples with 800 KeV protons. Protons with this energy react with $^{18}_0$ to produce $^{15}_N$ plus an $\alpha$ particle. The energy spectrum of the $\alpha$ particles recorded during proton irradiation was used to determine the $^{18}_0$ concentration profile. As a proton enters the sample, it loses energy as it interacts with the solid until it reacts with an $^{18}_0$ ion to produce an $\alpha$ particle. The initial energy of the $\alpha$ particle varies approximately linearly with impact energy of the proton. The $\alpha$ particle will also lose energy as it travels out of the sample. The energy of an $\alpha$ particle is thus a function of the location at which it originated, but it is not a simple function and obtaining a concentration gradient involves a complicated deconvolution. They prepared their samples by annealing single crystals of $\text{Al}_2\text{O}_3$ in $^{18}_0\text{O}_2$ enriched oxygen gas at a pressure of 1 atm. They hoped to eliminate any effect due to surface damage by using a cleaved surface. Between 1500°C and 1650°C their results were:

$$D = 8.5 \times 10^{-7} \exp(-78 \text{ kcal/mole/RT}) \text{cm}^2/\text{sec}$$
These results are about an order of magnitude lower with a slightly higher activation energy than the data that Oishi and Kingery call extrinsic.

The deconvolution of the α particle data to obtain the $^{18}O$ concentration profile seems susceptible to errors that would increase the uncertainty of the results. The gas-exchange reaction at the surface is a process that can also produce errors in the results.

All of the studies of oxygen diffusion shown that oxygen self-diffusivity is several orders of magnitude lower than the aluminum self-diffusivity found by Paladino and Kingery. It can also be concluded that oxygen diffusion is enhanced in grain boundaries.

**Indirect Methods**

Electrical conductivity, creep and sintering are processes that are diffusion controlled and thus, given an appropriate kinetic model, may be used to estimate self-diffusivities.

**Electrical Conductivity**

Electrical conductivity in ceramic materials can be electronic or ionic. Only ionic conductivity can be used to determine ionic diffusivities. Ionic conductivity has already been shown to be:

$$\sigma_i = c_i z_i^2 e^2 B_i$$  \hspace{1cm} \text{Eq. 1.35}

The mobility is related to the diffusivity by:

$$D_i = kTB_i$$  \hspace{1cm} \text{Eq. 1.36}
Frequently in the literature the lnσ is plotted against 1/T to give a straight line. In this case the mobility has the form:

\[ B = B_0 \exp\left(-\frac{Q_c}{RT}\right) \]  
\text{Eq. 2.1}

where \( B_0 \) is independent of temperature and \( Q_c \) is the activation energy for motion. In terms of this mobility the diffusivity will be:

\[ D = kT B_0 \exp\left(-\frac{Q_c}{RT}\right) \]  
\text{Eq. 2.2}

But \( D \) is usually given in the form:

\[ D = D_0 \exp\left(-\frac{Q_c}{RT}\right) \]  
\text{Eq. 2.3}

where \( D_0 \) is independent of temperature. To compare such conductivity data with diffusivity data ln(σT) must be replotted against 1/T. Alternatively, one can assume an average temperature in which case:

\[ Q_d = Q_c + RT_{av} \]  
\text{Eq. 2.4}

Substituting this value into Equation 2.2 and relating it to Equation 2.3 gives:

\[ D_0 = kT_{av} B_0 \exp(1) \]  
\text{Eq. 2.5}
Kingery and Pappis\textsuperscript{15} measured the electrical conductivity of Al\textsubscript{2}O\textsubscript{3} as a function of temperature and oxygen pressure. They found a minimum in electrical conductivity at an oxygen pressure of $10^{-5}$ atm. They attributed this to non-stoichiometry with holes conducting at high oxygen pressures and electrons at low oxygen pressures.

Özkan and Moulson\textsuperscript{16} developed a guarded electrode technique to eliminate the effects of surface and gas conduction. Using this technique, they measured the conductivity of single-crystal and polycrystalline alumina. They made no attempt to determine whether the conductivity was electronic or ionic. Their results show that most of the previous data was due to gas or surface conduction since those results were comparable with measurements they obtained from an air gap between electrodes. They also observed that the conductivity along the $c$ axis was about 50 times greater than that perpendicular to $c$. They reported an activation energy for conductivity of 4ev. Assuming an average temperature of 1100°C gives an activation energy for diffusion of 95 kcal/mole if is assumed that ionic conduction is predominant.

Brook, Yee and Kröger\textsuperscript{17} using a guarded electrode technique similar to that of Özkan and Moulson studied electrical conductivity as well as the emf generated by a difference in oxygen pressure across a sample. They concluded from the emf data that alumina is an ionic conductor at both high and low oxygen pressure. They concluded that $V_{Al}''$ vacancies were the rate controlling defect at high oxygen pressures with $Al_{i}'''$ interstitials controlling at low oxygen pressure.
It was later recognized\textsuperscript{18} that there was a basic error in their experimental apparatus. They had maintained the guard electrode at the wrong potential to eliminate surface and gas conduction effects for the emf studies. This invalidated their transference number results.

Kitazawa and Coble\textsuperscript{19} measured electrical conductivity in single crystal and polycrystalline Al$_2$O$_3$ using a sample configuration designed to eliminate gas and surface conduction. Their results showed that as the oxygen pressure was lowered, the conductivity decreased at first, then stayed constant, and finally increased at low oxygen pressures. The region which was independent of oxygen pressure was attributed to ionic conductivity while the oxygen dependent regions were attributed to electronic conduction. The region of ionic conductivity predominated at low temperatures but decreased as the temperature increased until it was completely eliminated above about 1600°C. The activation energy for ionic conduction was 57 kcal/mole which they concluded was that for extrinsic aluminum ion diffusion. They did not determine whether the dominant ionic species were an aluminum vacancy or an interstitial. This gives an activation energy for diffusion of 60 kcal/mole assuming an average temperature of 1100°C. They found that polycrystalline material exhibited electronic conduction over a wider range of temperatures.

Dutt, Hurrell and Kröger\textsuperscript{18} studied electrical conductivity and emf generated in Co-doped Al$_2$O$_3$ using a guarded electrode cell. They concluded that ionic conductivity dominated at low oxygen pressures with electronic conductivity dominating at high oxygen pressures.
They concluded that $\text{Al}_i^{i\cdots}$ interstitials were the principal charge carriers in the ionic region and holes in the electronic region.

Dutt and Kröger\textsuperscript{20} proposed that the conductivity measured by Pappis and Kingery could be ionic at low oxygen pressures. Since the Pappis and Kingery samples had 100 ppm iron, they concluded that $\text{Fe}_{\text{Al}}^X$ ions were reduced to $\text{Fe}_{\text{Al}}^+$ ions with $\text{Al}_i^{i\cdots}$ interstitials being produced to maintain charge neutrality.

**Creep**

In order to extract diffusivity information from creep data, it is necessary to establish that the deformation is due to diffusional creep and not to slip or some other non-diffusional controlled mechanism. Diffusional creep will be limited by the slower moving species.

Creep in polycrystalline $\text{Al}_2\text{O}_3$ occurs at a rate faster than is possible through control by the observed lattice diffusion of oxygen. However, the rate is in fair agreement with rates predicted from aluminum diffusion coefficients. Paladino and Coble\textsuperscript{21} extrapolated the Oishi and Kingery\textsuperscript{9} oxygen self-diffusion data in polycrystalline $\text{Al}_2\text{O}_3$ to smaller grain sizes and proposed that below a grain of 20\(\mu\), aluminum lattice diffusion would be slower than oxygen self-diffusion enhanced by grain boundaries. They thus concluded that diffusional creep in small grain size $\text{Al}_2\text{O}_3$ will be controlled by aluminum bulk diffusion with the oxygen diffusing through the grain boundaries. They observed that aluminum bulk diffusion was rate controlling even for a grain size of 34\(\mu\). They also concluded that at large grain sizes the oxygen boundary diffusion would be the rate limiting process.
Cannon and Coble\textsuperscript{22} reviewed diffusional creep in Al\textsubscript{2}O\textsubscript{3} and concluded that the creep results indicate that cation diffusivity is extrinsic for all materials tested and that it is increased for both divalent and tetravalent impurity additions. From the data reported for medium grain sized material, they concluded that for MgO-saturated Al\textsubscript{2}O\textsubscript{3}, the aluminum lattice diffusivity is:

\[
D^A_l = 1.36 \times 10^5 \exp(-138 \text{ kcal/mole}/RT) \text{ cm}^2/\text{sec}
\]

This activation energy would thus also contain the heat of solution for MgO in Al\textsubscript{2}O\textsubscript{3}. From the data for fine grained polycrystalline Al\textsubscript{2}O\textsubscript{3}, they find that the aluminum boundary diffusivity is rate controlling and is best given by:

\[
\delta D^b = 8.8 \times 10^{-4} \exp(-100 \text{ kcal/mole}/RT) \text{ cm}^2/\text{sec}
\]

This result is independent of the MgO concentration. From the creep rates of coarse-grained Al\textsubscript{2}O\textsubscript{3} they conclude that oxygen grain boundary diffusion is not rate limiting, but that at reasonable stresses a mechanism other than diffusional creep is involved. They suggested that the Nabarro climb mechanism could be involved at low stresses. Climb, which is also diffusion controlled, will be limited by the slower diffusing species in the lattice. The controlling diffusivity calculated from deformation data obtained by Heuer\textsuperscript{23} on single crystal Al\textsubscript{2}O\textsubscript{3} agrees with the oxygen self-diffusivity found by Oishi and Kingery\textsuperscript{9} if a climb controlled mechanism is assumed.
Lessing and Gordon\textsuperscript{24} suggest that for coarse-grained iron-doped material, aluminum lattice diffusion and oxygen boundary diffusion are comparable in magnitude.

\textit{Sintering}

Sintering, like creep, is controlled by diffusion of the slower moving species and, again like creep, is too fast to be attributed to control by oxygen lattice diffusion. Paladino and Coble\textsuperscript{11} calculated a diffusivity from sintering data which is within a factor of three of the aluminum self-diffusivity obtained by Paladino and Kingery.\textsuperscript{14} They thus conclude oxygen diffusion is more rapid in the boundaries and that aluminum bulk diffusion is rate limiting.

Fryer\textsuperscript{25} obtained activation energies for self-diffusion in $\text{Al}_2\text{O}_3$ from hot-pressing data. He studied undoped samples as well as MgO-doped and Ta$_2$O$_5$-doped materials.

The method he used was to measure the shrinkage rate of a compact during hot-pressing at a given temperature while 2-3\% densification took place. The pressure was removed from the compact and the temperature was lowered about 50\$C. After the system was allowed to come to thermal equilibrium, the pressure was again applied and the shrinkage rate was measured. Using a model he had developed for the final stage of hot-pressing, he calculated the diffusivities. The expression used was:

$$\frac{d}{dT}\left(\frac{\rho}{P}\right)^{\frac{3}{2}} = 4 \times 10^3 \frac{\sigma D \Omega \sigma}{k^2 k T}$$
where \( \rho \) is the density, \( P \) the fractional porosity, \( \sigma \) the applied pressure, \( l \) the mean pore separation, and \( \Omega_s \) the molecular volume. The activation energy was extracted from the two shrinkage rates observed with each sample. For an undoped sample he obtained a diffusivity of \( 4 \times 10^{-14} \text{cm}^2/\text{sec} \) at 1304°C with an activation energy of 115 kcal/mole. With an MgO-doped sample, he calculated a diffusivity of \( 5.1 \times 10^{-14} \text{cm}^2/\text{sec} \) at 1304°C with an activation energy of 130 kcal/mole and with a \( \text{Ta}_2\text{O}_5 \)-doped sample he calculated a diffusivity of \( 4.3 \times 10^{-14} \text{cm}^2/\text{sec} \) at 1382°C with an activation energy of 150 kcal/mole. By comparing these activation energies with the reported data he concluded that the undoped and \( \text{Ta}_2\text{O}_5 \)-doped diffusivities represented oxygen lattice diffusion control. He also concluded that the MgO-doped diffusivity represented aluminum lattice diffusion control. While the activation energies may be comparable with the oxygen diffusion data, the diffusivities are much too large. With the fine grain size of 1 \( \mu \)m which was reported, it would be expected that aluminum boundary diffusion would be the rate limiting process.

Defect Structure

Brook, Yee and Kröger\(^{17}\) proposed that a Frenkel disorder for the aluminum ions was most consistent with the oxygen pressure dependence that they observed for electrical conductivity. Hollenberg and Gordon\(^{26}\) observed that increasing the number of \( \text{Fe}^{2+} \) ions or the number of \( \text{Ti}^{4+} \) ions increased the creep rate. This was best explained by a Frenkel disorder among the aluminum ions, since \( V_{\text{Al}}'''' \) vacancies would predominate with \( \text{Ti}^{4+} \) doping and \( \text{Al}_i''' \) interstitials would
predominate with Fe$^{2+}$ doping. Dutt, Hurrell, and Kröger\textsuperscript{18} used optical absorption spectra, electron spin resonance, electrical conductivity and emf measurements on concentration cells to determine the defect structure in Co-doped Al$_2$O$_3$. They conclude that the Al$_i$···· interstitial was the main defect in their doped material. Dutt and Kröger\textsuperscript{20} proposed that the Pappis and Kingery\textsuperscript{15} electrical conductivity data can best be explained by a defect structure in which the Al$_i$···· interstitials are the major defect. Dienes et. al.,\textsuperscript{27} treating the bonding in Al$_2$O$_3$ as purely ionic, calculated the energies of formation and motion of the various simple point defects. The calculated energies of formation for the defects are:

\begin{align*}
V_{Al}^{'''} & \quad 9.1 \text{ eV/defect} \quad 210 \text{ kcal/mole} \\
Al_{i}^{'''} & \quad 10.8 \text{ eV/defect} \quad 249 \text{ kcal/mole} \\
V_{0}^{''} & \quad 3.5 \text{ eV/defect} \quad 80.7 \text{ kcal/mole} \\
O_{i}^{''} & \quad 10.5 \text{ eV/defect} \quad 242 \text{ kcal/mole}
\end{align*}

These energies indicate that the V$_{0}^{''}$ vacancies have the lowest energy of formation and thus would be the most abundant. Their result also indicates the V$_{0}^{''}$ vacancies will have the lowest energy of motion. These energies would indicate that oxygen self-diffusion would be much faster than aluminum self-diffusion which is not what has been observed. In view of this contradiction with observation, it must be concluded that these results are not valid.

Jones, Coble, and Mogab\textsuperscript{28} measured the diffusivity of a defect by color boundary migration in Ti-doped Al$_2$O$_3$. Their results were:

\[
d^\alpha = 430 \exp(-80 \text{kcal/mole}/RT) \text{cm}^2/\text{sec}
\]
They conclude that because the measured self-diffusivity of aluminum is two orders of magnitude higher than oxygen, this must be an aluminum vacancy. They make no assumption about the charge on the vacancy.

Dutt, Hurrell and Kröger measured a defect mobility in Co-doped Al₂O₃ at low oxygen pressure by electrical conductivity that they attributed to Al₁⁺⁺ interstitials. The value is:

\[ B_i = 1.22 \times 10^7 \exp(-3.97eV/kT) \text{cm}^2/\text{sec} \]

Assuming an average temperature of 1440°C gives a defect diffusivity of:

\[ D_i = 1.80 \times 10^6 \exp(-64.7 \text{cal/mole/RT}) \text{cm}^2/\text{sec} \]

Summary

It has been established by self-diffusion measurements that aluminum self-diffusion is several orders of magnitude faster in the bulk than oxygen self-diffusion. It has also been established by self-diffusion measurements that oxygen diffusion is enhanced in grain boundaries. This has been confirmed by creep and sintering measurements. The directly measured diffusivities as well as those extracted from conductivity, creep, and hot-pressing data are shown in Figure 2.1.

There is not sufficient data to firmly establish the defect structure of Al₂O₃. However, the available data does give a few clues. A theoretical calculation of the energies of formation of the possible defects indicates that Schottky defects would predominate. These
Figure 2.1
Measured Diffusivities in Al₂O₃
results must be considered in error since the predicted values for the
defect energies as well as their mobilities would require that oxygen
diffuse faster than aluminum. The observation of Hollenberg and Gordon
that the creep rate in $\text{Al}_2\text{O}_3$ was increased by the addition of either
titanium or iron can best be explained by a Frenkel disorder among
the aluminum ions. This means that the Schottky energy would be
greater than the Frenkel energy. If the mobility that Dutt, Hurrell,
and Kröger\textsuperscript{18} observed in Co-doped $\text{Al}_2\text{O}_3$ is that for the aluminum inter-
stitial, then:

$$\Delta H^i_m = 95\text{kcal/mole}$$

If the defect diffusivity that Jones, Coble and Mogab\textsuperscript{28} observed by
color boundary migration was that for the aluminum vacancy then:

$$\Delta H^{\nu\alpha}_m = 80\text{kcal/mole}$$

On the other hand, the activation energy that Kitazawa and Coble\textsuperscript{19}
obtained for ionic conductivity measurements gives:

$$\Delta H^i_m \text{ or } \Delta H^{\nu\alpha}_m = 60\text{kcal/mole}$$

There is not sufficient data to calculate the Schottky or Frenkel
energies.
From the data on the diffusion-controlled processes, it appears that oxygen self-diffusion is unimportant. Only in the case of deformation due to a climb mechanism or controlled by climb would it be rate controlling. Even though it appears to have little effect on any diffusion-controlled processes, it can be useful in determining the defect structure. Since the defects among the cations are coupled to those among the anions through the Schottky energy, an understanding of oxygen self-diffusion can be most useful in establishing the defect structure in $\text{Al}_2\text{O}_3$.

**ION PROBE MEASUREMENT OF SELF-DIFFUSION**

In systems which lack a suitable radio tracer, the recent availability of the ion probe provides a potential technique for direct measurement of self-diffusion in solids. This would eliminate many of the errors introduced by assumptions about surface reactions, nuclear reactions or particle energy distributions involved in the complicated procedures for measuring the $^{18}\text{O}/^{16}\text{O}$ ratio required previously. Although the ion probe has been available for over a decade, only in the past few years have techniques been developed for analysis of insulating materials on the probe. Even with the development of suitable techniques to prevent sample charging, little work has yet been done with the ion probe to measure self-diffusion in ceramic materials.

Coles and Long$^{29}$ used an ion probe to study the self-diffusion of Li in LiF. They prepared diffusion couples of $^{6}\text{LiF}$ and $^{7}\text{LiF}$. The samples were annealed long enough at each temperature to produce measurable diffusion over a distance of the order of 0.5mm. The annealed
samples were sectioned parallel to the diffusion direction and this surface was coated with a thin layer of aluminum to provide a conducting surface which prevented sample charging. The samples were analyzed on a Cameca ion probe in the microprobe mode. Measurements were made at 5, 10 or 25μm intervals across the couples using a beam of A⁺ ions. The primary beam had an energy of 11 keV, a diameter of 5μm and a current of 0.2 na. The secondary extraction potential was 6kv.

A W. Hofmann, et. al.30 used an ion probe to measure potassium self-diffusion in biotite. The biotite was sealed in a gold tube with a 2.0 normal alkali chloride aqueous solution that contained sodium, potassium and rubidium in proportions such that it would be in equilibrium with the biotite. The potassium in solution was enriched with 41K as a tracer. The charge was heated at 650°C and a pressure of 2.0 kbar for 41 days. The samples were analyzed on an ARL ion microprobe with 16O primary ions accelerated to 20 kb. The primary beam was focused to a diameter of 6μm and data was taken from a series of spots across the face of the sample. Data was taken from each spot as a function of time so that the diffusion could be measured in two dimensions. The beam was also rastered across an area 25μm x 20μm to erode the surface more evenly. They found that the self-diffusivity of potassium was about two to four orders of magnitude higher perpendicular to the c-axis than parallel to c.

It should be noted that in these two studies the ion probe was used in two different modes. As a microprobe, the composition of a surface is measured at specific location. In the sputtering mode,
the primary beam erodes the surface of material slowly exposing successive layers below the surface. The former is suitable for measuring diffusion depths that are large (at least several times the diameter of the primary beam). The latter technique is only suitable for shallow diffusion depths (a few micrometers at most). While the sputtering technique would be very sensitive to near-surface artifacts such as absorption of impurities, segregation, or mechanical damage, the microprobe technique would be less so. The sputtering technique also contains errors due to non-ideal crater geometry: that is, the crater bottom may not be flat and the sides of the crater may also contribute to the signal. Rastering of the primary beam, as done by Hofmann, et. al., is a technique which produces nearly ideal crater geometry.

Hofmann, et. al., measured diffusion in two dimensions by combining the two techniques. Since the craters that were produced were probably far from ideal, their results undoubtedly contained a large error. However, their procedure does show the versatility of the ion probe. It should, in fact, be possible to measure composition gradients in three dimensions.
III. OBJECTIVES

This work has several objectives. The first is to measure the self-diffusion of oxygen in $\text{Al}_2\text{O}_3$ as a function of temperature. A solid-state diffusion experiment was planned to eliminate the possibility of error due to a surface reaction which is present in gas-exchange experiments.

Since it has been observed that damage is done to the surface of a crystal by mechanical polishing, it is the objective of this work to establish the extent of that damage and its influence in diffusion rates. It is also intended that a technique be developed to prevent or eliminate that damage. Damage-free samples are to be analyzed along with surface-damaged samples to determine the effect of the damage.

The M.I.T. ion probe is to be used to analyze the penetration of $^{18}O$ into the samples. It is also the object of this work to participate in development of the instrument. Electronic controls were designed and constructed for tuning the spectrometer and stabilizing the primary current. General help was provided in assembling, testing, and developing techniques for use of the instrument.

This work is also aimed at assessing the general value of using an ion probe to study oxygen self-diffusion. This would indicate the feasibility of using an ion probe in other studies of ceramic materials.
IV. EXPERIMENTAL PROCEDURE

CONSTRUCTION OF M.I.T. ION PROBE

Because of the many problems inherent in the techniques previously used to study oxygen self-diffusion in $\text{Al}_2\text{O}_3$, the availability of an ion probe at M.I.T. provided an excellent opportunity to obtain much more reliable data. Help was provided in the construction of the probe in order to expedite the availability of the instrument for analyses. A mass control unit was designed and built to produce the required magnetic and electric fields in the spectrometer for a selected mass. A filament control unit for the duoplasmatron primary ion source was designed and built to stabilize the primary ion current. These devices are described in Appendices II and III. Help was also provided in the assembling and testing of the probe including the development of techniques for his use.

SELECTION OF EXPERIMENTAL CONDITIONS

It was decided that the tracer would be applied to the samples from a solid $^{18}\text{O}$-enriched $\text{Al}_2\text{O}_3$ film. This is a technique that had been successfully used in the past. A solid state source of tracer was selected to eliminate any influence of a surface reaction which will be present in a gas exchange experiment. Because of the limited amount of tracer that could be applied to the samples, the diffusion penetrations would have to be shallow (less than 1 $\mu$m) to maintain an $^{18}\text{O}$ gradient that could be observed. Under these conditions the ion
probe would have to be used in the eroding mode. Since the sputtering rate of \( \text{Al}_2\text{O}_3 \) is slow, it was necessary to keep the maximum measurable tracer penetration to about 5,000Å. While these shallow penetrations are much more sensitive to the surface state, they are accomplished with shorter annealing times. The shorter anneals permit a wider temperature range to be studied. The temperature range studied extends from 1585°C to 1840°C. To guarantee that the oxygen in the film is exchanged only with the sample, the diffusion anneals were done in a vacuum of better than \( 10^{-5} \) torr.

**SAMPLE PREPARATION**

**Material**

The samples were all cut from one single-crystal boule of \( \text{Al}_2\text{O}_3 \) grown by the Czochralsky technique at Union Carbide Corporation, San Diego, California. They were cut into \( 1 \text{cm} \times 1 \text{cm} \times 2 \text{mm} \) plates with the large faces perpendicular to the growth direction of the boule. The orientation of the large faces was determined using the back-reflection Laue technique to be within 2° of a \{1102\} plane. A quantitative spectrochemical analysis done by the Strnad Spectrographic Laboratory at M.I.T. indicated that the samples contained 9ppm Fe, 11ppm Si and less than 1ppm each Cu and Mg.

**Surface Preparation**

Prior to application of the tracer film, it was necessary to polish the sample surface. Hockey\(^3\) and others\(^32, 33\) have reported that a damaged layer of less than 1\(\mu\)m depth results from mechanical polishing.
The damage appeared as dislocations confined to narrow randomly oriented linear regions with the enclosed areas containing few dislocations. These narrow regions appeared to be the remains of scratches. They also reported that the damage can essentially be removed by annealing. Hockey observed that the damage could be significantly reduced by annealing at 1200°C in air for one hour. Reismann, et. al.,\textsuperscript{32} reported that annealing in air for four hours at 1500°C essentially removed any damage. Work was done to verify these results. Two samples were polished beginning with 10-30μm diamond paste on a rotating brass wheel covered with photographic paper (nap side up). The particle size of the diamond paste was systematically reduced during polishing. A final polish was provided with 0-1μm diamond paste. One of the polished specimens was annealed in air at 1650°C for four hours, following which both specimens were etched in phosphoric acid at 420°C for three minutes. The annealed sample showed a dislocation density near the native dislocation density of 10^3/cm^2 while the unannealed sample revealed much damage. A micrograph of this surface is shown in Figure 4.1. The damage is indicated by large agglomerations of etch pits and long scratch-like grooves. It was therefore concluded that damage free samples could be prepared by mechanical polishing followed by an anneal in air at 1650°C for four hours.

One face of each sample was polished to a scratch free finish at the G.T.E. Laboratory in Waltham, Massachusetts. After polishing, one half of the samples were annealed in air at 1650°C for four hours. The remaining samples were not annealed so that the effect of the damage on the experiment could be assessed.
Figure 4.1

Mechanical Damage Done to Surface During Polishing
Tracer Application

A thin film of tracer was applied to the polished surface of the specimens by the successive deposition and oxidation in $^{18}O_2$ of an aluminum film. The formation of a protective oxide layer on aluminum metal results in a limiting oxide thickness of about $200\AA^{34,35}$ at $600^\circ$C. The oxidation of an aluminum surface takes place by the nucleation of crystallites of $Al_2O_3$.\textsuperscript{35} As oxidation proceeds the crystallites grow across the surface while maintaining a nearly constant thickness. Once the crystallites impinge, the oxidation process effectively stops. The thickness of the crystallites is controlled by the diffusion of oxygen from the surface along the edge of the crystallites. As the temperature increases, the growth rate of the crystallites increases faster than the diffusion of oxygen along the edge of the crystallites so that the limiting thickness of the oxide film decreases with increasing temperature. Because the limiting thickness was only about $200\AA$, the process was repeated from five to ten times to obtain the desired thickness.

Aluminum films, $100\AA$ thick, were vapor deposited in a vacuum system consisting of an Ultek #20-360 ion pump and an Ultek #214-4000 titanium sublimation pump which maintained the pressure at less than $10^{-6}$ torr during deposition. A Sloan model BXV-6 electron beam gun was used to vaporize an ingot of 99.9999% pure aluminum obtained from the A. D. MacKay Corporation of New York City. The thickness of the aluminum film was monitored during deposition by a Granville-Phillips series 219 film thickness monitor.
The films were oxidized for 24 hours at 520°C in 90-99% $^{18}O_2$ enriched 99.5% pure $O_2$ gas at between 100 torr and 500 torr. The gas was obtained from Mound Laboratory of the Monsanto Research Corporation. The oxidizing apparatus is shown in Figure 4.2. The lecture bottle contained the $^{18}O_2$ gas. The three flasks contained Linde molecular sieve, type 5A. The samples to be oxidized were placed in a Vycor tube surrounded by the Kanthal wound furnace. Once the samples were in the proper position, the Vycor tube was closed and the system was evacuated by immersing pumping flask 1 in liquid $N_2$. The pressure was monitored using a Bendix GT-340 thermistor vacuum gauge. A vacuum of better than $10^{-2}$ torr could be achieved using the molecular sieve. Pumping flask 2 was intended for back-up if necessary. Once the pressure was below $10^{-2}$ torr, the flask was valved off and the system was flooded with $^{18}O_2$ from the lecture bottle. The system pressure was brought to between 100 torr and 200 torr and the furnace was raised to 520°C. After 24 hours the furnace was turned off and the storage flask was immersed in liquid $N_2$ to collect the $^{18}O_2$. Once the gas was collected in the molecular sieve, the flask was valved off. In this way the isotope could be used for more than one oxidation run. The system was then opened to remove the samples. The process was repeated by inserting the samples, sealing the system and then immersing flask 1 in liquid $N_1$ to evacuate the system. Once the system was evacuated, the flask was valved off, the storage flask was removed from liquid $N_2$, and opened to let the $^{18}O_2$ back into the system.
Figure 4.2
Oxidizing Apparatus

Kanthal Wound Furnace

Thermistor Vacuum Gauge Head

Storage Flask

Pumping Flask 2

Pumping Flask 1

Lecture Bottle

Flasks Containing Molecular Sieve

$^{18}O_2$ Supply
The thickness of the $\text{Al}_2\text{O}_3$ film was calculated by using the density of aluminum metal, the density of $\text{Al}_2\text{O}_3$ and the weight percent of aluminum in $\text{Al}_2\text{O}_3$. The $\text{Al}_2\text{O}_3$ film thickness is 1.3 times the aluminum film thickness. Since the deposition-oxidation process was repeated five to ten times, the samples were prepared with $\text{Al}_2\text{O}_3$ films ranging from 650Å to 1300Å. The film thickness for each sample is shown in Table 4.1.

Extrapolating the Oishi and Kingery low temperature diffusion data\textsuperscript{9} to 520°C gives an oxygen self-diffusivity of less than $2 \times 10^{-23}$ cm$^2$/sec. This should represent an upper limit to the diffusivity. A rough estimate of the extent of diffusion is given by $4\sqrt{Dt}$. Since $4\sqrt{Dt} < 0.4\text{Å}$, there was effectively no diffusion of $^{18}\text{O}$ into the samples during the oxidation of the aluminum films.

**Diffusion Anneal**

Following the application of the tracer films, the samples were annealed in pairs in a vacuum for times ranging from one hour at 1839°C to 9 1/2 days at 1584°C. A pre-annealed sample and an as-polished sample were annealed together. The anneals were done in a Brew model 1068 vacuum furnace which maintained the pressure at less than $10^{-5}$ torr during the anneal. The temperature of the furnace was brought to 1200°C over the period of an hour in order to keep the pressure in the furnace from rising too high. The temperature was raised from 1200°C to the desired annealing temperature within one minute. The temperature was maintained to ±5°C by a Leeds and Northrup series 60 control unit maintaining constant power to the furnace.
The samples were placed with the tracer films together on top of a single-crystal setter cut from the same boule. The samples were covered by a small tantalum box with a small hole in the side. The box with the hole provided near block-body conditions for measurement of the temperature. The temperature was measured with a Leeds and Northrup number 8622-C optical pyrometer by sighting on the hole in the box through a port in the furnace. The error due to losses in the quartz window in the port were measured using a pyrometer calibrating bulb. The temperature measurements were corrected for the observed error. The temperature and annealing times of the samples are shown in Table 4.1.

**SAMPLE ANALYSIS**

**Specimen Preparation**

To facilitate the use of the ion probe, the samples were coated with a thin film of aluminum metal (500Å to 800Å). The aluminum film provided a conducting surface to maintain the sample at a constant potential and it also aided in focusing the primary beam. A filament was also used to spray the sample with electrons in order to prevent sample charging. The filament was supplemental to the aluminum film. The probe worked with either the aluminum film or the filament. However, the greatest stability was achieved with the combination.

**Focusing Primary Beam**

In order to interpret data obtained from an ion probe used in the eroding mode, it is necessary to relate the signal to the composition at a desired depth. If the crater produced by the primary beam is flat with straight sides then all the signal corresponds to the
Table 4.1

Film Thickness, Annealing Temperature, & Annealing Time

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Film Thickness</th>
<th>Temperature</th>
<th>Annealing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 &amp; 6</td>
<td>1170Å</td>
<td>1839°C</td>
<td>1.1 hrs.</td>
</tr>
<tr>
<td>2 &amp; 7</td>
<td>650Å</td>
<td>1742°C</td>
<td>2.0 hrs.</td>
</tr>
<tr>
<td>3 &amp; 8</td>
<td>780Å</td>
<td>1676°C</td>
<td>9.9 hrs.</td>
</tr>
<tr>
<td>4 &amp; 9</td>
<td>910Å</td>
<td>1620°C</td>
<td>74.0 hrs.</td>
</tr>
<tr>
<td>5 &amp; 10</td>
<td>1040Å</td>
<td>1584°C</td>
<td>257.6 hrs.</td>
</tr>
</tbody>
</table>

Samples 1-5 are pre-annealed.
composition at the bottom of the crater. If the crater has sloping sides, then the signal also contains a component due to the composition of the sides. In order to minimize this error, the sides of the crater should be as steep as possible. This requires a sharply focused, uniformly illuminated spot from the primary beam.

A zinc sulfide crystal was used as a fluorescent screen for focusing the primary beam. The beam was initially focused on the ZnS and the blue spot produced by the beam was observed in an optical microscope attached to the ion probe. The primary beam was focused to give a uniform spot about 100µm in diameter. Once the spot appeared well focused on the ZnS, the Al₂O₃ sample was moved into position.

The aluminum film was observed through the microscope. As the aluminum film was eroded away by the ion beam, the position of the crater could be seen. The evenness with which the film was sputtered away indicated how flat-bottomed the crater would be. If the size of the crater grew with time, this indicated that the beam was not sharply focused. The length of time required to sputter through the aluminum film was also noted. This time varied from 30 sec. to 2 min. depending on the primary beam current. This is the time at which the surface of the Al₂O₃ crystal becomes exposed.

Data Collection

Once the condition of the primary beam was determined to be suitable for obtaining meaningful data, the sample was moved so that the primary beam hit an undisturbed area in the center of the sample. After allowing the elapse of the time that has been noted as necessary to
sputter through the aluminum film, the abundance of mass 16 and mass 18 were measured as a function of time.

The electron multiplier used as a detector in the ion probe produces a pulse for each ion transmitted by the spectrometer. Thus the number of counts produced by the probe was related to the abundance of ions of the selected mass. In order to eliminate any error arising from inability to locate precisely the peak maximum, the mass peaks were integrated by counting while the spectrometer was scanned over the mass number of the desired peak. The mass scanning rate was constant. Since the two peaks could not be examined at the same time, the order of scanning was reversed to compensate for a change in concentration. That is, the mass 16 peak was scanned followed by a scan of mass 18; then mass 18 was scanned followed by mass 16, and so on. In this way the error caused by the time delay in the two readings were averaged out.

Data Reduction

The craters were examined with a Carl Zeiss dual-beam interference microscope. The average depth of the crater was measured. The ratio of the length of the crater to the width was measured as was also the ratio of width of the sides to the length of the crater. Interference micrographs for samples 1 and 5 are shown in Figure 4.3. The sputtering rate which was taken to be constant, was obtained from the crater depth divided by the sputtering time.

The peak widths are proportional to the mass. The relationship between peak width and mass can be illustrated by considering the
Figure 4.3

Interference Micrographs of Craters
equation that describes the operation of the mass spectrometer (see Appendix I):

\[ \frac{M}{q} = \frac{R_m^2 B^2}{R_e \xi} \]  
\text{Eq. 4.1}

Since the particles entering the spectrometer enter over a range of angles and since the entrance and exit slits have a finite width, \( R_m \), the radius of the magnetic sector has a range \( \Delta R_m \) and \( R_e \), the radius of the electrostatic sector, has a range \( \Delta R_e \). The range of mass that will be transmitted can then be described by:

\[ \Delta M = \frac{2R_m q B^2}{R_e \xi dR_m} - \frac{R_m^2 q B^2}{R_e \xi dR_e} \]  
\text{Eq. 4.2}

Substituting Equation 4.1 into Equation 4.2 gives:

\[ \Delta M = (2\Delta R_m / R_m - \Delta R_e / R_e) M \]  
\text{Eq. 4.3}

thus showing that the peak width is proportional to the mass. Because the mass peaks are integrated, the broadening effect must be accounted for. To standardize the peaks, the mass 16 counts were multiplied by 18/16. The concentration of \(^{18}\text{O}\) is thus (mass 18 counts)/(18/16 mass 16 counts + mass 18 counts).

Correction for Non-Ideal Crater

Under ideal conditions (a flat-bottomed crater with straight sides), only material from a single depth is sputtered by the primary beam. However, under real conditions the crater has sloping sides from which material is also sputtered. In this case, the signal con-
tains components from a range of depths. Since the signal contained a component due to the composition of the sides of the crater, the data had to be adjusted to obtain the true concentration profile of the tracer.

A correction can be made by considering an equation that describes the signal from the ion probe:

\[
\sigma_m = \frac{\dot{m}^*}{\dot{m}} = \frac{\int_A \sigma_B(x,y)I(x,y)\,dA}{\int_A I(x,y)\,dA} \tag{Eq. 4.4}
\]

\(\sigma_m\) is the mole fraction of isotope measured, \(\dot{m}^*\) is the sputtering yield of \(^{18}\text{O}\), \(\dot{m}\) is the total sputtering yield for oxygen, \(\sigma_B(x,y)\) is the concentration of \(^{18}\text{O}\) on the surface exposed to the primary beam with an intensity \(I(x,y)\). It is assumed that the ionization probability for \(^{18}\text{O}\) is the same as that for \(^{16}\text{O}\). The integrals are taken over the area illuminated by the primary beam.

A model was developed to solve this expression by assuming a uniform cylindrical primary ion beam with Gaussian edges. In one dimension this can be described by:

\[
I = I_o \exp\left(-\frac{x^2}{a^2}\right) \quad x \leq 0
\]

\[
I = I_o \quad 0 < x \leq 2R \quad \tag{Eq. 4.5}
\]

\[
I = I_o \exp\left\{-\left(\frac{x-2R}{a}\right)^2\right\} \quad x \geq 2R
\]

where \(R\) is the radius of the beam and \(a\) is a parameter indicating the sharpness of the edge. This is shown in Figure 4.4. If the sputtering rate is assumed proportional to the beam intensity, then the pit shape
caused by a beam normal to the sample can be described in one dimension by:

\[ h = h_B \exp(-x^2/a^2) \quad x \leq 0 \]
\[ h = h_B \quad 0 \leq x < 2R \quad \text{Eq. 4.6} \]
\[ h = h_B \exp\{- (x-2R)^2/a^2\} \quad x \geq 2R \]

where \( h_B \) is the depth of the crater. This is shown in Figure 4.5.

By using the symmetry of the crater, Equation 4.4 can be solved in one dimension by considering rings around the crater. This gives:

\[
\sigma_m = \frac{\pi R^2 c(h_B) I_o + 2\pi \int_0^\infty (R+x)c(h) I_o \exp(-x^2/a^2) \, dx}{\pi R^2 I_o + 2\pi \int_0^\infty (R+x) I_o \exp(-x^2/a^2) \, dx} \quad \text{Eq. 4.7a}
\]

or, by evaluating the integral in the denominator and dividing through by \( \pi R^2 I_o \):

\[
\sigma_m = \frac{c(h_B) + \frac{2}{\alpha R} \int_0^\infty (R+x)c(h) \exp(-x^2/a^2) \, dx}{1 + \frac{2}{\alpha R} \frac{1}{\sqrt{\pi} + \frac{\alpha R}{\alpha R}}} \quad \text{Eq. 4.7b}
\]

In the M.I.T. ion probe the primary beam strikes at an angle of near 45°. In this case the shape of the crater formed is elliptical and the shape of the sides can be described as in Equation 4.6 with \( \alpha \) a function of the position around the crater. To keep the solution tractable, an average \( \alpha \) is used and the ratio of \( \frac{\alpha}{\alpha} \) is assumed constant. That is if along the major axis of length 2A:

\[ h = h_B \exp(-x^2/a^2) \quad x \leq 0 \quad \text{Eq. 4.8} \]
Figure 4.4
Primary Beam Intensity

Figure 4.5
Crater Depth
and along the minor axis length 2B:

\[
h = h_B \exp\left(-\frac{y^2}{b^2}\right) \quad y \leq 0 \quad \text{Eq. 4.9}
\]

then:

\[
a/A = b/B \quad \text{Eq. 4.10}
\]

This is shown in Figure 4.6. With these modifications, Equation 4.7 becomes:

\[
c_m = \frac{c(h_B) + \frac{2}{AB} \left[ \frac{A^2 + B^2}{2} \right] \int_0^\infty (1 + \frac{x}{A}) c(h) \exp\left(-\frac{x^2}{a^2}\right) dx}{1 + \frac{A}{A} \left[ 1 + (\frac{A}{B})^2 \right] \left( \sqrt{\pi + \frac{A}{A}} \right)} \quad \text{Eq. 4.11a}
\]

If \( \beta = \left[ \frac{1 + (A/B)^2}{2} \right]^{1/2}, \zeta = a/A \text{ and } \eta = x/a \text{ then:} \)

\[
c_m = \frac{c(h_B) + 2\zeta \beta \int_0^\infty (1 + \zeta \eta) c(h) \exp\left(-\eta^2\right) d\eta}{1 + \beta \sqrt{\pi + \zeta}} \quad \text{Eq. 4.11b}
\]

It should be noted that the two parameters that are needed are \( a/A \) the sides to axis ratio and \( A/B \) the ratio of the major to minor axis. For discrete data points, this can be approximated by:

\[
c_{m^i} = \frac{c_i + 2\zeta \beta \sum_{j=1}^{J} c_j \hat{H}_j}{1 + \beta \sqrt{\pi + \zeta}} \quad \text{Eq. 4.12}
\]
Figure 4.6
Crater Geometry

\[ \frac{a}{A} = \frac{b}{B} \]
where $c_{mi}$ is the $i^{th}$ data point, $c_i$ is the mole fraction at that depth and $H_j$ is the integral:

$$H = \int_{u}^{v} (1+\zeta \eta) e^{\exp(-\eta^2)} d\eta$$

taken between the limits bounding the $j^{th}$ data point. For $j=1$

$$u = \frac{\eta_1 + \eta_2}{2} \quad \text{and} \quad v = \infty$$

for $i > j > 1$

$$u = \frac{\eta_j + \eta_{j+1}}{2} \quad \text{and} \quad v = \frac{\eta_j + \eta_{j-1}}{2}$$

for $j = i$

$$u = 0 \quad \text{and} \quad v = \frac{\eta_i + \eta_{i-1}}{2}$$

By Equation 4.8

$$h_j = h_{\xi} e^{\exp(-x_j^2/a^2)} = h_{\xi} e^{\exp(-\eta^2)}$$

where $j < i$

so that

$$\eta_j = \left\{ \ln(h_{\xi}/h_j) \right\}^{\frac{1}{2}}$$
Rearranging Equation 4.12 gives:

\[ a_i = \frac{\{1+\xi B(\sqrt{n}+\xi)\}c_{m_i}-2\xi B \sum_{j=1}^{i-1} c_j^2}{(1+2\xi BH_i)} \]  

Eq. 4.13

Using this expression, the data can be corrected point by point. Assuming that \( a_1 = a_1 \), \( a_2 \) is calculated. Knowing \( a_1 \) and \( a_2 \), \( a_3 \) is determined and so on until all the data has been corrected.

CURVE FITTING TO THE THICK FILM SOLUTION

A best fit of the adjusted data is found by minimizing the sum of the squares of the deviation. The deviation is given by:

\[ \epsilon_i = \frac{c - d}{\sqrt{\pi} x_i^2} \exp(-n^2) \, dn - a_i \]  

Eq. 4.14

where \( a_i \) is the adjusted value of concentration. For a best fit:

\[ \sum_i \epsilon_i^2 = \text{minimum} \]  

Eq. 4.15

This is achieved if:

\[ \frac{\partial}{\partial D} \left[ \sum_i \epsilon_i^2 \right] = 0 \]  

Eq. 4.16

The derivative is given by:

\[ \frac{\partial}{\partial D} \left[ \sum_i \epsilon_i^2 \right] = \frac{c}{2\sqrt{\pi} D^3} \sum_i \left[ (c_0 P_i/\sqrt{n} - a_i) c_0 \right] \]  

Eq. 4.17
where:

\[
F_i = \frac{x_i + d}{2\sqrt{Dt}} \exp\left(-\eta^2\right) d\eta
\]

and:

\[
G_i = (x_i + d)\exp\left\{-\frac{(x_i + d)^2}{4Dt}\right\} - (x_i - d)\exp\left\{-\frac{(x_i - d)^2}{4Dt}\right\}
\]

Since the value for \(\sigma_o\) is also uncertain, it was also included in the fitting process by:

\[
\frac{\partial}{\partial \sigma_o} \left[ \sum_i \varepsilon_i^2 \right] = \frac{2}{\sqrt{\pi}} \sum_i (c_i F_i / \sqrt{\pi} - c_i) (F_i) = 0 \quad \text{Eq. 4.18}
\]

This reduces to:

\[
c_o = \sqrt{\pi} \sum_i c_i F_i / \sum_i F_i^2 \quad \text{Eq. 4.19}
\]

Combining Equations 4.16, 4.17, and 4.19 gives:

\[
\sum_i c_i G_i = \left[ \sum_i F_i G_i \right] \left[ \sum_i c_i F_i / \sum_i F_i^2 \right] \quad \text{Eq. 4.20}
\]

This expression does not have an explicit closed form solution, but can easily be evaluated by computer. This was done by adjusting the value for \(D\) until the two sides of Equation 4.20 were equal.
VERIFICATION OF ION PROBE DATA CHARACTERISTICS

There are a number of assumptions made in interpreting the ion probe data. First, it was assumed that the primary ion beam does not appreciably change the composition profile of the sample under analysis as a result of ions near the surface being driven into the sample by the primary ions. To establish the validity of this assumption and to test the procedure for data reduction, a sample was analyzed that had been coated with a tracer film but which had not been annealed. Correction for contributions from the sides of the crater for this sample provided very good agreement with the known step-distribution of isotope. This is seen in Figure 4.7. The large tail on the data indicates that the crater geometry is far from ideal. Even with this poor crater, the corrected data showed a sharp step in composition. Much better craters were obtained in analyzing the annealed samples. This is one verification that the correction procedure does work and that it even works with poor craters. The observed step in concentration also established that the composition profile was not being significantly modified by the primary ions.

Another assumption that was made is that the ionization probability of $^{18}O$ is the same as $^{16}O$. This assumption was verified by analyzing an unenriched sample of $Al_2O_3$. It was observed that the ratio of the $^{18}O$ signal to the total oxygen signal was 0.002 ± 0.001. The naturally occurring abundance of $^{18}O$ is 0.002. For this to be true, the ionization probabilities would have to be the same. The imprecision in the data at the low $^{18}O$ concentrations was due to the low count rates.
Figure 4.7
Ion Probe Data for Unannealed Film
V. EXPERIMENTAL RESULTS

The data for the five pre-annealed samples were analyzed using the computer program which corrected the data for the contribution from the sides of the craters. A diffusion coefficient was then obtained by minimizing the mean square deviation of the corrected data to the "thick film solution." The correcting and fitting procedure was described in the previous chapter. The results are shown in Figures 5.1 through 5.10. In Figures 5.1 through 5.5, the raw data is shown along with the corrected data. The best fit curve to the corrected data for the thick film solution is provided and is labeled "CONCENTRATION PROFILE." The curve labeled "CORRECTED PROFILE" is the profile obtained by reversing the correction procedure on the "CONCENTRATION PROFILE." The "CORRECTED PROFILE" is the profile provided by the correcting procedure to the raw data. In Figures 5.6 through 5.10, the raw data is shown along with the "CORRECTED PROFILE" shown in Figures 5.1 to 5.5. Also included in these figures is the best fit curve to the raw data for the thick film solution. This curve is labeled "UNCORRECTED PROFILE." The correction of the data was done using the two parameters, the sides to axis ratio and the major to minor axis ratio, taken from the interference micrograph of the craters. Because of aberrations in the primary beam, the geometry of the craters varied from that assumed in the model used in the correction procedure. Because of the deviations of crater geometry as well as the lack of
Figure 5.2
Ion Probe Data for Sample 2
Figure 5.3
Ion Probe Data for Sample 3
Figure 5.5
Ion Probe Data for Sample 5
Figure 5.8
Ion Probe Data for Sample 3
Figure 5.9
Ion Probe Data for Sample 4
Figure 5.10  
Ion Probe Data for Sample 5
precision in measuring the crater parameters, those parameters were adjusted and the data re-analyzed to provide the best fit to the data. The best fit is obtained by minimizing the mean square deviation of the raw data from the "CORRECTED PROFILE." The effect of the adjustment of these parameters on the value of $D$ that is extracted is rather small. There is less than a factor of 2 difference between the corrected and the uncorrected values.

A satisfactory fit for the as-polished samples could not be obtained for the thick film solution by using the applied thickness of the tracer films. It was found, however, that a good fit could be obtained by assuming a film thickness of about 500Å to 1000Å thicker than the actual applied thickness with a correspondingly smaller initial concentration. These results are shown in Figures 5.11 to 5.14. In these figures the raw data is shown along with the corrected data. Also shown are the best fit curves to the raw data. These curves are obtained by reversing the correction procedure on the calculated composition profile. The curve labeled "APPLIED FILM" is the best fit obtained using the applied thickness of the tracer film. The curve labeled "ADJUSTED PROFILE" is the best fit obtained by adjusting the tracer film thickness. This increased film thickness could be accounted for by the presence of enhanced diffusion through a damaged surface layer corresponding to the increased thickness. If the diffusivity in the surface layer were larger than the bulk diffusivity then the composition in this damaged layer would become homogenous before there were significant diffusion into the bulk. This would broaden the
Figure 5.11
Ion Probe Data for Sample 6.
Figure 5.12
Ion Probe Data for Sample 7
Figure 5.13
Ion Probe Data for Sample 8
Figure 5.14
Ion Probe Data for Sample 10
effective thickness of the initial film. While Hockey concluded that the damaged layer was less than \( \mu m \) (he did not attempt to indicate a lower limit), these results indicate that the thickness of the damaged layer was from 500Å to 1000Å. The exact thickness of the damaged layer is not clear however, since the damage is undoubtedly being annealed out as diffusion progresses.

After analyzing sample #9, the crater was observed to be unacceptable for providing reliable data. Since the remaining as-polished samples were consistent in showing the effect of the surface damage, it was felt that it was unnecessary to re-analyze the sample on the ion probe.

An eleventh sample with a 1300Å tracer film was annealed at 1700°C for 27 hours. This sample was annealed by itself with the tracer film uncovered. Following the anneal all \(^{18}O\) concentrations were found to be near the natural occurring abundance of 0.2%. This was undoubtedly due to evaporation during the anneal. The effect of evaporation on the normal samples was therefore examined. Using the simple Langmuir evaporation model, the flux leaving the surface into a vacuum is:

\[
J = \alpha P(M/2\pi RT)^{1/2}
\]

Eq. 5.1

Here \( P \) is the equilibrium vapor pressure of the material, \( M \) its molecular weight and \( \alpha \) the vaporation coefficient. For the uncovered sample, the material loss rate will be this flux times the area of the surface which is 1cm\(^2\). Using reported values\(^{36} \) for \( P=2 \times 10^{-7} \) atm and \( \alpha=.14 \) at 1700°C, predicts the evaporation of material 145\(\mu m \) thick in
27 hours. This could certainly account for why so little tracer could be detected. The reported values for partial pressures of Al₂O₃ indicate that the pressure increases more slowly with temperature than the diffusivity of oxygen. This means that while the evaporation rate may decrease with temperature, the increased annealing times would allow more material to evaporate. There is no indication in the data to indicate that more material had evaporated during the lower temperature anneals than during the highest temperature anneal. Considering the amount of tracer in the samples, it was also apparent that much evaporation had not taken place. It must therefore be concluded that covering the samples sufficiently reduced the effect of evaporation.

It should be noted that the total amount of tracer in an as-polished sample is significantly greater than that in the corresponding pre-annealed sample. Since the tracer films were applied simultaneously to the pre-annealed and as-polished samples, the amount of tracer should be the same in each after the diffusion anneal. The difference observed must be due to vapor transport of tracer from one sample to the other. It should be noted that the as-polished samples show a dip in the concentration at the surface, and that the surface concentrations for a set of samples are about the same. These observations along with the rate of evaporation indicate that the vapor transport between samples is fast so the two samples could be considered to be one with a single tracer film in the center. The damaged layer on the as-polished half would then result in the tracer film broadening while the center of mass of the tracer shifts into the as-polished crystal. This devia-
tion from the thick film boundary conditions should be kept in mind as a source of error because it not only reduces the effective initial concentration of the film in the pre-annealed samples but it will change the shape of the profile.

The diffusivities obtained from all the samples are summarized in Table 5.1. Also shown is the ratio of the amount of tracer in the as-polished samples to that in the pre-annealed samples.

It should be noted that the diffusivity for the as-polished samples using the applied film thickness is slightly greater than that obtained from the pre-annealed samples. This increased diffusivity is what would be expected to result from the enhanced diffusion in the damaged layer. The diffusivity obtained from the as-polished samples by adjusting the tracer film thickness to give the best fit to data is lower than that obtained from the pre-annealed samples. This reduced diffusivity results from an effective reduction in diffusion time due to the broadening of the film. It is probably not too meaningful, however, to try and extract any quantitative results from the as-polished data since the condition of the damaged layer is not constant. It does, however, definitely establish that surface preparation has a pronounced effect on shape of the concentration gradient and thus on the diffusion coefficient which is deduced. A gas exchange experiment would be particularly sensitive to the damaged layer since the enhanced diffusion would increase the total amount of tracer in the samples and not just change the composition profile.
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Corrected $D$ (cm²/sec)</th>
<th>Uncorrected $D$ (cm²/sec)</th>
<th>Temperature (°C)</th>
<th>$\frac{\alpha_a}{\alpha_p}$</th>
<th>Sample Number</th>
<th>Corrected $D$ (cm²/sec)</th>
<th>Uncorrected $D$ (cm²/sec)</th>
<th>Temperature (°C)</th>
<th>$\frac{\alpha_a}{\alpha_p}$</th>
<th>Sample Number</th>
<th>Corrected $D$ (cm²/sec)</th>
<th>Uncorrected $D$ (cm²/sec)</th>
<th>Temperature (°C)</th>
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<td>$1.03 \times 10^{-16}$</td>
<td>$1.50 \times 10^{-16}$</td>
<td>1620</td>
<td>*</td>
<td>9</td>
<td>*</td>
<td>*</td>
<td>1620</td>
<td>*</td>
<td>9</td>
<td>*</td>
<td>*</td>
<td>1620</td>
<td>*</td>
</tr>
<tr>
<td>5</td>
<td>$4.48 \times 10^{-17}$</td>
<td>$8.65 \times 10^{-17}$</td>
<td>1584</td>
<td>1.3</td>
<td>10</td>
<td>$7.33 \times 10^{-17}$</td>
<td>$1.23 \times 10^{-17}$</td>
<td>1584</td>
<td>1.3</td>
<td>10</td>
<td>$7.33 \times 10^{-17}$</td>
<td>$1.23 \times 10^{-17}$</td>
<td>1584</td>
<td>1.3</td>
</tr>
</tbody>
</table>

$\alpha_a = \text{Amount of tracer in as-polished samples}$

$\alpha_p = \text{Amount of tracer in pre-annealed samples}$
The diffusion anneal was done in a vacuum to eliminate any exchange of the $^{18}O$ in the samples with the atmosphere during the anneal. This was necessary since the amount of material in a film a few hundred angstroms thick is quite small. Because the anneals were done in a vacuum furnace the oxygen partial pressure was unknown. The total pressure was between $10^{-6}$ torr and $10^{-5}$ torr in the furnace throughout the anneals. The tantalum box enclosing the samples would also keep the oxygen partial pressure quite low in the vicinity of the samples. The oxygen partial pressure is therefore unknown but low. However, at the surface with the tracer film, the oxygen partial pressure should be the equilibrium oxygen partial pressure as previously indicated. For a low oxygen partial pressure, any deviation from stoichiometry would result in an increase in the oxygen vacancy concentration. This increase in oxygen defects would thus increase the diffusivity.

Using the method of least squares to provide a best straight line fit of $\log D$ vs $1/T$, the diffusivity is given by:

$$D = 6.4^{+3.1}_{-5.3} \times 10^5 \exp(-188\pm7 \text{kcal/mole}/RT) \text{cm}^2/\text{sec}$$

The logarithm of $D$ is plotted against $1/T$ in Figure 5.15. Also plotted in Figure 5.10 are the results of Oishi and Kingery$^9$ for single crystals and the results of Reddy and Cooper.$^{11}$

It should be noted that the results of the present work are lower than the results of Oishi and Kingery by a factor of more than 30. The activation energy of the present work is slightly higher than that in
Figure 5.15
Oxygen Self-Diffusion in $\text{Al}_2\text{O}_3$
the high temperature region of the Oishi and Kingery data and much higher than that for their low temperature data as well as the results reported by Reddy and Cooper. The low activation energies and higher diffusivities reported by these workers could be accounted for by a damaged layer near the surface. Oishi and Kingery reported that samples pre-annealed at 1900°C showed diffusivities comparable with that given for the high temperature region. Reddy and Cooper reported that the surfaces they used were cleaved. A cleaved surface, however, may not necessarily be damage free.

Since the oxygen pressure of the present measurements is unknown, it is difficult to correlate the results with earlier measurements. However, if the impurity concentration is high enough, the impurities will dominate the defect concentrations. The major impurities are 11 ppm of silicon and 9 ppm of iron. Dutt and Kröger maintain that iron in Al₂O₃ is mostly Fe³⁺ with a small amount becoming Fe²⁺ in reducing atmospheres. Assuming that Frenkel defects for aluminum predominate, the reactions are given by:

\[ \text{Fe}_2\text{O}_3 = 2\text{Fe}_{\text{Al}} + 3\text{O}_0 \]

\[ \text{Al}_{\text{Al}} + \frac{3}{2}\text{O}_0 + 3\text{Fe}_{\text{Al}} = 3\text{Fe}_{\text{Al}'}, \text{Al}'', \ldots + \frac{3}{4}\text{O}_2 \]

The silicon going into solution is given by:

\[ 3\text{SiO}_2 = 3\text{Si}_{\text{Al}}' + \text{V}_{\text{A}'''} + 6\text{O}_0 \]
If $[\text{Fe}^{3+}] \gg [\text{Fe}^{2+}]$ as suggested by Dutt and Kröger, then the silicon will dominate the defect concentration. Even if all the iron were in the reduced state as might be expected to compensate the silicon impurities, the silicon would still dominate the defect concentrations. For temperatures below which the intrinsic aluminum vacancy concentration is much less than the concentration of silicon impurities, then the defect formation will be controlled by the silicon impurity concentration.

If the aluminum vacancy concentration $[\text{V}_{\text{Al}}']$ is fixed by the impurity level, the oxygen vacancy concentration is given by:

$$[V_0'] = \frac{3}{[\text{Si}]} \exp(-\Delta G_s/3RT)$$

Where $\Delta G_s$ is the free energy of formation of Schottky defects. The activation energy for oxygen diffusion is then given by (See Equation 1.32):

$$Q = \frac{\Delta H_s}{3} + \Delta H_m = 188 \text{ kcal/mole}$$

where $\Delta H_s$ is the heat of formation for Schottky defects and $\Delta H_m$ is the activation barrier for oxygen diffusion. Again it should be kept in mind that this will only be true if the aluminum vacancy concentration is fixed.

It should also be kept in mind that these diffusivities were measured normal to the (1102) plane. The diffusivity is a tensor given by:
For $A_1$, $D_{11}=D_{22}=D_{a}$ is the diffusivity in the basal plane, and $D_{33}=D_{c}$ is the diffusivity normal to the basal plane and parallel to the $c$ axis. The observed diffusivity is given by:

$$D = \lambda_i \lambda_j D_{ij} \quad \text{Eq. 5.3}$$

where $\lambda_i$ and $\lambda_j$ are the direction cosines with respect to the appropriate axes. In terms of the diffusivities normal to and parallel to the $c$ axis, the observed diffusivity is given by:

$$D = .713D_{a} + .287D_{c}$$
VI. CONCLUSIONS

A static primary ion beam focused to a uniformly illuminated spot about 100μm in diameter can be used to erode the surface of a sample in order to measure the composition as a function of depth ranging from 100Å to 10,000Å. The true composition may be extracted from isotope ratios produced by this spot, by means of a correction developed to account for the portion of the signal contributed by the sides of the crater. It is therefore concluded that the ion probe is a suitable instrument for measurement of oxygen diffusion in Al₂O₃.

The results obtained for anion self-diffusion in samples of single-crystal Al₂O₃ annealed in a 10⁻⁵ torr vacuum over a temperature range of 1585°C to 1840°C are given by:

\[ D = 6.4^{+31.0}_{-5.3} \times 10^5 \exp(-188±7\text{cal/mole/RT})\text{cm}^2/\text{sec} \]

This diffusivity is in the direction normal to a \{1102\} plane. This is considered to be extrinsic. It was also concluded that the state of mechanical damage of the surface affects the diffusion rates. Samples which were pre-annealed to remove surface damage done by mechanical polishing showed a considerably different tracer diffusion profile than samples that were not pre-annealed. This was accounted for by enhanced diffusion through a damaged layer of the order of 0.1μm thick.
VII. SUGGESTIONS FOR FUTURE WORK

The samples in the present work were annealed in vacuum to prevent exchange of the tracer with the atmosphere. This has made the results difficult to compare with previous measurements. Procedures should be developed which would allow the samples to be annealed in an atmosphere of known oxygen partial pressure. The effect of oxygen pressure on diffusion would be very helpful in determining the defect structure of $\text{Al}_2\text{O}_3$.

Since a static primary beam in the ion probe was used to analyze the samples, the data had to be corrected, which introduced some uncertainty into the results. Measurements should be made using a rastered primary beam to produce a flat-bottomed crater and an aperture to eliminate any signal due to the sides of the crater, once these features become available on the M.I.T. ion microprobe.

Work might also be done to attempt to observe intrinsic self-diffusion in $\text{Al}_2\text{O}_3$ by going to higher temperatures with ultra-pure crystals. Alternatively, measurements on samples of varying impurity levels would also be useful in determining the defect structure and defect energies in $\text{Al}_2\text{O}_3$.

The diffusivity as a function of crystallographic direction is something that could be studied to provide insight into the mechanism of diffusion.
Now that the ion probe has been established as a suitable tool for studying oxygen self-diffusion, it may be employed to study aluminium self-diffusion in \( \text{Al}_2\text{O}_3 \), as well as isotopic diffusion in a wide variety of materials not amenable to analysis by other techniques.
APPENDIX I

DESCRIPTION OF THE M.I.T. ION PROBE

The M.I.T. ion probe can be divided into two parts. The first is the primary column where the primary ions are generated, formed into a beam and focused. The second part is the mass spectrometer where the secondary ions sputtered by the primary ion beam are analyzed.

PRIMARY COLUMN

The primary ions are generated in a hot filament duoplasmatron ion source. In the duoplasmatron, a plasma is produced by an arc in a rarified inert gas atmosphere ($10^{-1}$ torr). The arc is maintained by the emission of electrons from a heated filament. The degree of ionization in the plasma is a function of the power dissipated by the arc. The ions are extracted through a small aperture by an extraction electrode at a high voltage (to 20kv). The movement of the ions in the plasma is biased toward the aperture by a magnetic field thus increasing the output of ions from the duoplasmatron. Argon is the gas usually used in the M.I.T. probe. However, nitrogen and krypton have also been successfully used. In the present work a filament control unit was constructed for the M.I.T. ion probe to stabilize the primary beam current. This is done by maintaining the power dissipated by the arc at a constant value (see Appendix III).
The primary beam is focused by two electrostatic lenses to uniformly illuminate a spot on the sample. The upper lens produces an image of the duoplasmatron aperture at a distance below the lens which depends on its focal length. The focal length is set by the voltage on the lens. Neglecting aberrations, the size of the image is the image-distance (the distance between the lens and the image produced) divided by the object-distance (the distance between the duoplasmatron aperture and the lens) times the size of the aperture. The focal length of the bottom lens can be adjusted so that the image produced by the upper lens is focused on the sample. The size of the spot on the sample is the image distance of the bottom lens (the distance from the bottom lens to the sample) divided by the object distance (the distance from the image formed by the upper lens to the bottom lens) times the size of the image formed by the upper lens. Thus a spot can be produced from less than 1μm to greater than 100μm in diameter.

In practice, spherical aberration dominates the optical performance and therefore the above description is only a qualitative approximation. An aperture is placed in front of the bottom lens to reduce spherical aberration. By uniformly illuminating this aperture by means of the top lens and by focusing the image of the aperture on the sample, the best crater geometry is obtained. There is another aperture between the duoplasmatron and the upper lens that allows the primary column to be differentially pumped so that a high vacuum can be maintained in the spectrometer. This aperture does not affect the optics of the primary ion beam.
There are two sets of deflection plates between the two lenses which are used to deflect the primary beam. There are two sets (one above the other) for deflection in one direction and two sets for deflection at a right angle to that direction. By deflecting the beam twice, the deflected beam can be kept parallel to the undeflected beam, which eliminates any aberrations due to the deflection.

MASS SPECTROMETER

A Dual Double-Focusing Mass Spectrometer

The spectrometer in the M.I.T. ion probe is a dual double-focusing mass spectrometer (Figure A1.1). A double-focusing mass spectrometer consists of an electrostatic sector which is kinetic energy selective and a magnetic sector which is momentum selective. A combination of the two is mass selective. This can be demonstrated by considering the behavior of a charged particle in an electric and a magnetic field.

In a radial electric field, the trajectory of a charged particle is given by:

\[ \frac{Mv^2}{R} = q\xi \]  \hspace{1cm} Eq. A1.1

or:

\[ \frac{Mv^2}{2q} = \frac{(KE)}{q} = R \frac{\xi}{2} \]

M is the mass of a particle with charge q and velocity v, \( \xi \) is the
Figure A1.1
M.I.T. Ion Probe
magnitude of the electric field, \( R_e \) is the radius of the trajectory and \( KE \) is its kinetic energy. In the M.I.T. ion probe the electrostatic sector consists of two concentric cylindrical plates (See Sectors 1 and 4 in Figure A1.1). A radial electric field is therefore produced between the plates whose magnitude is proportional to the voltage between the plates. The energy of the transmitted particles is therefore proportional to the voltage between the plates. In a homogeneous magnetic field, the path of a charged particle is given by:

\[
\frac{Mv^2}{R_m} = qvB
\]

or

\[
\frac{Mv}{q} = \frac{P}{q} = R_mB
\]

where \( P \) is the momentum of the particle, \( R_m \) is the radius of its path and \( B \) is the magnetic field. Combining Equations A1.1 and A1.2 gives:

\[
\frac{M}{q} = R_m^2B^2/R_eE
\]

If the dispersion of the magnetic sector is equal and opposite that of the electrostatic sector, the spectrometer is double focusing. By placing two double-focusing mass spectrometers in tandem as in the M.I.T. ion probe, the error due to gas scattering in the spectrometer can be reduced.
There are four electrostatic lenses in the spectrometer of the M.I.T. ion probe to focus the ions and give better resolution and higher transmission.

Output Signal

A Faraday cup is provided so that the current due to the transmitted particles can be measured directly. A more sensitive detection system is also provided which uses a deflection plate to deflect the transmitted ions into an electron multiplier. The electron multiplier produces a current pulse for each ion detected. The pulses can then be counted by an electronic counter to give the abundance of a desired mass. A ratemeter is also provided to give a voltage which is a function of the abundance (the count rate).

Mass-Selection Control Unit

A mass-selection control unit was designed and constructed in the present work to control the magnetic and electric fields in the appropriate sector as indicated by Equation A1.3. The control unit sets the sample potential with respect to the spectrometer. Since the secondary ions are accelerated by the voltage on the sample into the spectrometer, the kinetic energy of the particles in the spectrometer is a linear function of the sample potential. The lens voltages which depend on the kinetic energy of the particles are also adjusted by the control unit as is the voltage on the deflection plate for the electron multiplier.

The mass-selection control unit also linearizes the magnetic field. The magnetic field for the magnetic sector is produced by a
large electromagnet which is non-linear with respect to the current producing the field. There is also hysteresis associated with the magnet. A Hall effect probe is used to monitor the field and provide the necessary feedback so that the magnetic field will be proportional to a reference level.

The control unit also allows the mass to be scanned at a constant rate. By selecting the desired mode on the front panel either the electric field is fixed while the magnetic field is scanned or the magnetic field is fixed while the electric field is scanned.
APPENDIX II

DESIGN AND CONSTRUCTION OF MASS-SELECTION CONTROL UNIT

The mass-selection control unit sets the fields and voltages in the mass spectrometer which are required for the transmission of particles of a selected mass. The magnetic field in the magnetic sectors, the electric field in the electrostatic sectors, the sample potential and the voltages in the four electrostatic lenses and the deflection plate at the detector are the variables that must be adjusted to tune the spectrometer. The control unit was designed and built to set those variables so that the spectrometer can select masses of less than 1 amu to more than 200 amu and can scan any range of mass within those limits at a constant rate.

MASS REFERENCE LEVEL

The control unit produces a voltage that is proportional to the mass to charge ratio of the particles to be analyzed. A schematic of the mass reference level control circuitry is shown in Figure A2.1. The "mass zero" control is a coarse adjustment of the mass reference level and serves to set the lowest mass in an automatic mass scan. The "fine tuning" control provides a fine adjustment of the mass selected. The voltage selected by the "fine tuning" adjustment is added to the mass scan level in "op amp" A1. The output of A1 is attenuated by the "mass range" control before it is added to the "mass zero" level in amplifier A2 to provide the mass reference.
Figure A2.1
Mass Reference Level Circuitry
level. The "mass range" control thus determines the sensitivity of the "fine tuning" control and the "mass scan level". The output of Al is also provided at a connector on the rear panel of the control unit to supply the x-axis voltage level for an x-y recorder (the y-axis is the output of the spectrometer).

The mass scan level which scans the mass at a constant rate is produced by the mass scan circuitry shown by a block diagram in Figure A2.2. An astable multivibrator oscillating at a constant frequency is used as a fixed clock. A monostable multivibrator is used to shape the output of the astable multivibrator to give narrow clock pulses. A variable clock rate is obtained by counting the fixed clock pulses with a 10 bit digital counter. By selecting one of the output bits or the fixed clock directly with the "scan rate" switch, the fixed clock rate is divided by $2^n$, where $n$ ranges from 0 to 10. The clock pulse is again shaped by a monostable multivibrator. The "start/stop" pushbutton sets or resets a bistable multivibrator (flip flop) which is used to gate the clock pulse. If the output of the "flip flop" is high, the start/stop light will be lit and the clock pulse will pass through the nor gate. If the "flip flop" is low, then the clock pulse cannot get past the gate. The variable clock pulse goes to 10 bit up/down digital counter (one that counts up and down instead of counting up and then resetting to zero). The "up/down" pushbutton reverses the direction of counting and the "reset" pushbutton resets the counter to zero. The digital output of the counter is fed into a digital to analog (D/A) converter which
Figure A2.2
Mass Scan Level Circuitry
produces a voltage proportional to the digital output of the counter. The mass scan level is the output of the D/A converter.

FIELD CONTROL LEVELS

As indicated by Equation A1.3 the mass of a transmitted particle in the mass spectrometer is proportional to the square of the magnetic field in the magnetic sectors and inversely proportional to the electric field in the electrostatic sectors. The kinetic energy of the transmitted particles are proportional to the electric field. To properly adjust these fields using the mass reference level, analog multiplier modules were used. The field control level circuitry is shown in Figure A2.3. In the analog multipliers used, the relationship between the voltages at the three terminals \( x \), \( y \), and \( z \) are given by:

\[
v_z = \frac{v_x v_y}{10}
\]

The mass reference level is applied to the \( y \) terminal of analog multiplier M1 and the energy reference level is applied to the \( x \) terminal. The \( z \) terminal then becomes the \( "B^2" \) reference level.

The "reference" control sets a voltage that is applied to the non-inverting input of "op amp" A1, whose output is the energy reference level. If the "scan mode" switch is in the magnetic scan position then the output of the amplified is fed back to the inverting input making it a unity gain amplifier. The energy reference level is then set by the "reference" control. As the mass reference level is changed, the "\( B^2 \)" level will change accordingly while the
Figure A2.3

Field Control Levels Circuitry
The energy reference level stays fixed. If the "scan mode" switch is in the electric scan position the the $B^2$ level is applied to the inverting input of the "op amp" and the energy reference level is adjusted to make the $B^2$ reference level equal to that set by the "reference" control. In this case, as the mass reference level varies, the energy reference level will vary while the $B^2$ level stays fixed.

The $B^2$ level is applied to the $z$ terminal of a second analog multiplier M2. The output is taken from the combined $x$ and $y$ terminals giving the square root which is the magnetic field reference level. Amplifier A2 is a buffer that prevents M2 from being loaded.

The energy reference level is used to control the electric field in the electrostatic sectors as well as the voltages on the electrostatic lenses and the deflector. Since all these are proportional to the energy reference level, "op amps" are used to provide the proper constants of proportionality. The electric field control circuitry is shown in Figure A2.4. Since the kinetic energy of the particles entering the spectrometer is that gained by being accelerated from the sample potential plus the secondary energy of the sputtered ions, the sample potential is linearly related to the energy reference level. The mass selection control unit subtracts a level set by the "energy offset" control from the energy reference level using an "op amp" to control the sample potential. In this way the whole energy spectrum of the secondary ions can be analyzed.
Electric Field Control Circuitry

Figure A2.4
FIELDS PRODUCED

The magnetic field is produced by a large electromagnet. As with all electromagnets with ferromagnetic cores, the field is a non-linear function of the current. The mass selection control unit was designed to maintain a magnetic field in the spectrometer which is proportional to the magnetic reference level. The magnet control circuitry is shown in Figure A2.5. The magnet is driven by a Spectromagnetic Industries Model 6000 current regulated power supply. The output current of the supply is controlled by a reference input voltage. The magnetic field is monitored by F. W. Bell Model 8860 Field Detector with a Model STB8-0402 Hall Effect Probe which produces a voltage proportional to the magnetic field. The output of the field detector is applied to the inverting input of an "op amp", with the magnetic reference level applied to the non-inverting input. The output of the amplifier provides the input voltage for the magnet power supply and is set to maintain the magnetic field, as measured by the field detector, the same as the magnetic field reference level. To stabilize the feedback arrangement and prevent it from oscillating, the voltage on the magnet was fed back through capacitor C2 and resistor R4.

The electric fields in the electrostatic sectors are produced by two high voltage power supplies. A CPS model 5001 PR supplies 0 to +5kv and a CPS model 5001 NR supplies 0 to -5kv. The positive voltage supply is used for the other plate. The supplies drive
Figure A2.5
Magnet Control Circuitry
one electrostatic sector directly and a voltage divider network is used to provide the voltages for the other sector.

The lenses and the deflection plate get their voltages from a voltage divider network driven by a 0 to 20 kv CPS Model 1200 PR power supply. The sample voltage is provided by a separate CPS Model 1200PR 0 to 20 kv power supply.
In a duoplasmatron ion source, a rarified gas is ionized by an arc discharge. The degree of ionization is a function of the arc voltage and current. In the M.I.T. ion probe, the arc is maintained by the electron emission of a heated filament. The arc conditions are a function of the electron emission from the filament and the emission is a function of the filament temperature which, in turn, is a function of the power dissipated by the filament. Upon aging, the filament deteriorates and its resistance increases. If the filament is powered by a constant voltage, then, as it ages, the current and the power will decrease causing a reduction in the ionization of the gas in the duoplasmatron. To keep the primary ion current constant, a filament control unit was designed and built to keep the voltage and current of the arc constant.

A schematic of the filament control circuitry is shown in Figure A3.1. The filament voltage is supplied by a Kepco Model JQE 6-22M power supply. The filament supply is used in a voltage programmed mode where the output voltage is proportional to an input voltage. The current in the arc is supplied by a Hewlett-Packard Model 6299A power supply used in the current regulated mode (the current does not vary with changing load conditions). The arc voltage which is the output voltage of the current regulated supply
is monitored using a voltage divider network R1 and R2. The output of the voltage divider is applied to the non-inverting input of "op amp" Al whose inverting input is fixed by R4, the "voltage reference" control. The output of the amplifier drives the input of the filament supply. In this arrangement, the filament voltage will vary to maintain the output of the arc voltage divider equal to that set by the "voltage reference" control, thus maintaining the arc voltage constant. Capacitor C1 and resistor R1 adjust the gain and bandwidth of the circuitry to prevent oscillation. The intermediate electrode which is ferro-magnetic aids in striking the arc as well as shaping the magnetic field to maximize the ion output. Zener Diodes D1 and D2 provide protection from high voltage arcs in the spectrometer which can produce large transients that can damage the circuitry.
APPENDIX IV
DATA REDUCTION PROGRAMS

MAIN PROGRAM

PROGRAM SOLVE

C
C THIS PROGRAM ANALYSES THE ION PROBE DEPTH PROFILE
C DATA FOR A STATIC BEAM.
C
C INPUT IS FROM DEVICE 6.
C
C IF SWITCH 1 IS UP NO CRATER CORRECTION WILL BE MADE.
C
C IF SWITCH 3 IS UP THE INDIVIDUAL DATA POINTS WILL
C NOT BE PROVIDED. IF THE SWITCH IS UP THE OUTPUT IS ON
C DEVICE 6 BUT IF IT IS DOWN THE OUTPUT IS ON DEVICE 5.
C
DIMENSION NTM(100), NO16(100), NO18(100), XFRAC(100),
1 CM(100), CALC(100), C(100)
BYTE DFILE(10)
BYTE TODAY(9)
BYTE FF
DATA FF/12/
DATA YES/'YES'/
CALL DATE(TODAY)
WRITE(6, 420)
READ(6, 440) DFILE
CALL ASSIGN(1, DFILE, 10)
IN=0
SRTWO=SQRT(2.0)
SRPI=SQRT(3.1415926536)
CALL SSWTCH(1, NN)
2 IPAGE=1
WRITE(6, 100)
READ(6, 120) FTHK
WRITE(6, 140)
READ(6, 120) XBOT
IF(NN.EQ.2) GOTO 3
SAX=0.
AXRAT=1.
GOTO 4
3 IF(IN.EQ.1) GOTO 44
WRITE (6, 160)
READ (6, 125) AXRAT
WRITE (6, 180)
READ (6, 125) SAX
RCON = SQRT ((AXRAT * AXRAT + 1.) / 2.)
COFN = 1. + SAX * RCON * (SRPI + SAX)
IF (IN. NE. 0) GOTO 17
WRITE (6, 240)
READ (6, 120) ANTM
DO 5 I = 1, 100
READ (1, 260) NTM(I), NO16(I), NO18(I)
IF (NTM(I).LT.0) GOTO 10
TOT = 18. * NO16(I) / 16. + NO18(I)
C018 = NO18(I)
5 CM(I) = C018 / TOT
WRITE (6, 280)
NDATA = I - 1
DO 15 J = 1, NDATA
15 XFRAC(J) = (1. * NTM(J)) / (1. * NTM(NDATA))
CONTINUE
IF (NN. NE. 1) GOTO 19
DO 18 J = 1, NDATA
18 C(J) = CM(J)
GOTO 44
19 C(1) = CM(1)
20 DO 40 J = 2, NDATA
JNL = J - 1
SIDES = 0.
DO 30 K = 1, JNL
RUL = 4.
IF (K. GT. 1) RUL = SQRT (ALOG (2. * XFRAC(J)) / 
1 (XFRAC(K - 1) + XFRAC(K)) )
RLL = SQRT (ALOG (2. * XFRAC(J) / (XFRAC(K) + XFRAC(K + 1))))
30 SIDES = SIDES + FACT (RLL, RUL, SAX) * C(K)
RLL = 0.0
RUL = SQRT (ALOG (2. * XFRAC(J) / (XFRAC(J) + XFRAC(J - 1))))
DENOM = 1. + 2. * SAX * RCON * FACT (RLL, RUL, SAX)
C(J) = (COFN * CM(J) - 2. * SAX * RCON * SIDES) / DENOM
40 CONTINUE
44 DTMIN = 1.
DTMAX = 1. E20
IF (IN. EQ. 0) DT = 1. E10
MAX = 0
MIN = 0
45 SRDT = SQRT (DT)
SCDIR = 0.0
SADIR = 0.0
SCA = 0.0
SASQ=0.0
DO 50 J=1,NDATA
XDIF=XFRAC(J)*XBOT
XPF= XDIF+FTHK
XMF= XDIF-FTHK
XPFN= XPF/(2.0*SRDT)
XMFN= XMF/(2.0*SRDT)
DIREV=XPF*EXP(-XPFN*XPFN)-XMF*EXP(-XMFN*XMFN)
AREAJ=THKFLM(XMFN, XPFN)
SCDIR=SCDIR+C(J)*DIREV
SADIR=SADIR+AREAJ*DIREV
SCA=SCA+C(J)*AREAJ
50 SASQ=SASQ+AREAJ*AREAJ
DFF=SCDIR-SCA*SADIR/SASQ
IF(ABS(DFF).LT.0.000001) GOTO 52
IF(DFF.LT.0.0) DTMIN=DT
IF(DFF.LT.0.0) MIN=1
IF(DFF.LT.0.0) FFMIN=DFF
IF(DFF.GT.0.0) DTMAX=DT
IF(DFF.GT.0.0) MAX=1
IF(DFF.GT.0.0) FFMAX=DFF
IF(DTMAX/DTMIN.LT.1.000001) GOTO 52
IF(MN.EQ.1) GOTO 51
MN=0
51 MN=MN+1
IF(MN.EQ.1.AND.MAX.EQ.1.AND.MN.EQ.1)
1 DT=(FFMAX*DTMIN-FFMIN*DTMAX)/(FFMAX-FFMIN)
IF(MIN.EQ.1.AND.MAX.EQ.1.AND.MN.EQ.1)
1 DT=(DTMAX+DTMIN)/2.
IF(MIN.EQ.0.AND.MAX.EQ.0) DT=2.0*DTMIN
IF(MIN.EQ.0.AND.MAX.EQ.1) DT=DTMAX/2.0
GOTO 45
52 FNORM=FTHK/(2.0*SRDT)
CZERO=SRPI*SCA/SASQ
CSURF=CZERO*THKFLM(-FNORM,FNORM)/SRPI
CALL SSWTCH(3,NP)
IF(NP.EQ.1) GOTO 55
WRITE(5,460)DFILE,TODAY,IPAGE
LINE=0
WRITE(5,300)FTHK, XBOT, ANTM, AXRAT, SAX
WRITE(5,320)
55 SERR=0.
SERSQ=0.0
DO 60 J=1,NDATA
XDIF=XFRAC(J)*XBOT
XNORM= XDIF/(2.0*SRDT)
A=XNORM-FNORM
B=XNORM+FNORM
CALC(J)=CZERO*THKFLM(A,B)/SRPI
IF(NN.NE.1) GOTO 56
CALCM=CALC(J)
GOTO 58

56  RLLH=SQRT(ALOG(2.*XFRAC(J)/XFRAC(1)))
SIDES=0.
DO 57 K=1,J
RUL=RLLH
IF(K.GT.1) RUL=SQRT(ALOG(2.*XFRAC(J)/
   1 *(XFRAC(K-1)+XFRAC(K))))
RLL=0.
IF(K.LT.J) RLL=SQRT(ALOG(2.*XFRAC(J)/
   1 *(XFRAC(K)+XFRAC(K+1))))
57  SIDES=SIDES+FACT(RLL, RUL, SAX)*CALC(K)
SIDES=SIDES+FACT(RLLH, 4., SAX)*CSURF
CALCM=(CALC(J)+2.*SAX*RCON*SIDES)/COFN

58  ERR=CM(J)-CALCM
SERR=SERR+ERR
SERSQ=SERSQ+ERR*ERR
IF(NP.EQ.1) GOTO 60
IF(LINE.LT.40) GOTO 59
LINE=0
IPAGE=IPAGE+1
WRITE(5,480) FF
WRITE(5,460) DFILE, TODAY, IPAGE
WRITE(5,320)
59  WRITE(5,340) XDIFCM(J),CALCMC(J),CALC(J)

60  LINE=LINE+1
AERR=SERR/NDATA
AERSQ=SERSQ/NDATA
STDEV=SQRT(AERSQ-AERR*AERR)
DIF=DT*1.OE-16/ANTM
DD=2.0*SQRT(DT)
NF=5
IF(NP.EQ.1) NF=6
WRITE(NF,360) DIF, DD, CZERO, CSURF, STDEV
IF(NP.NE.1) WRITE(5,480) FF
WRITE(6,370)
READ(6,380) FIN
IF(FIN.EQ.YES) STOP
IN=1
CALL SSWTCH(1,NN)
IF(NN.EQ.1) GOTO 2
WRITE(6,400)
READ(6,380) CHANGE
IF(CHANGE.EQ.YES) IN=2
GOTO 2

100  FORMAT('*FILM THICKNESS=')
FUNCTION PROGRAM FACT

FUNCTION FACT(A, B, SAX)

C
A PROGRAM TO EVALUATE THE COEFFICIENTS NEEDED TO
C CORRECT THE ION PROBE DATA.
C
FACT=0.
IF(B.GT.4.) B=4.
IF(A.GT.4.) RETURN
R=(B-A)*5.
N=R+1
DELTA=(B-A)/(2.*N)
DO 10 L=1,N
RLLF=A+2.*DELTA*(L-1)
RULF=A+2.*DELTA*L
XFIX=(RLLF+RULF)/2.
CDEL1=2.*((1.+SAX*XFIX))
CDEL3=2.*((2.*XFIX*XFIX-1.)*(1.+SAX*XFIX))
1 -2.*SAX*XFIX/3.

120 FORMAT(F10.0)
125 FORMAT(F10.6)
140 FORMAT('DEPTH=')
160 FORMAT('AXIS RATIO=')
180 FORMAT('SIDE/AXIS=')
240 FORMAT('ANNEALING TIME=')
260 FORMAT(3I10)
280 FORMAT(' DIMENSION EXCEEDED')
300 FORMAT(5X, 'FILM THICKNESS=',F8.0, 'A', 9X, 'PIT DEPTH=',
1 F8.0, 'A'/5X, 'ANNEALING TIME=',F8.0, 1X, 'SEC', 5X,
2 'A/B=',F5.3, 5X, 'SIDES/AXIS=',F5.3/>
320 FORMAT(10X, 'X', 15X, 'C(APARENT)', 16X, 'C(FACTUAL)/
1 9X, '(A)', 8X, '(MEASURED)', 1X, '(CALCULATED)', 3X,
2 'MEASURED)', 1X, '(CALCULATED)/')
340 FORMAT(5X, F8.0, 8X, F8.6, 4X, F8.6, 5X, F9.6, 4X, F8.6)
360 FORMAT(//5X, 'D=', E9.3, X, 'CM*CM/SEC', 10X,
1 'DIFFUSION DISTANCE=',F8.0, 'A'/7X, 'CO=',
2 'F8.6, 4X, 'C(O)=',F8.6, 4X, 'STDEV=', E2.6///)
370 FORMAT('*FINISHED? ')
380 FORMAT(A3)
400 FORMAT('*CHANGE CRATER PARAMETERS? ')
420 FORMAT('*WHICH DATA FILE? ')
FUNCTION PROGRAM THKFLM

FUNCTION THKFLM(A,B)

C A PROGRAM TO EVALUATE THE THICK FILM SOLUTION TO FICK'S SECOND LAW AT THE POSITION X.
C A=(X-THK)/2*SGRT(DT) AND B=(X+THK)/2*SGRT(DT)
C THK IS THE THICKNESS OF THE TRACER FILM, D IS THE DIFFUSION COEFFICIENT AND T IS THE ANNEALING TIME

THKFLM=0.
IF(B.GT.4.) B=4.
IF(A.GT.4.) RETURN
R=(B-A)*5.
N=R+1
DELTA=(B-A)/(2.*N)
DO 10 L=1,N
RLLF=A+2.*DELTA*(L-1)
RULF=A+2.*DELTA*L
XFIX=(RLLF+RULF)/2.
CDEL3=2.*(2.*XFIX*XFIX-1.)/3.
CDEL5=(4.*XFIX**4-12.*XFIX*XFIX+3.)/15.
CDEL7=(8.*XFIX**6-60.*XFIX**4+90.*XFIX*XFIX-15.)/315.
10 THKFLM=THKFLM+EXP(-XFIX*XFIX)*(DELTA*CDELI
1 +CDEL3*DELTA**3+CDEL5*DELTA**5+CDEL7*DELTA**7)
RETURN
END
REFERENCES


BIOGRAPHICAL NOTE

The author was born in Salt Lake City, Utah on September 5, 1942. He attended public schools in Salt Lake City and graduated from South High School in 1960. He graduated magna cum laude from the University of Utah with a B. S. degree in Electrical Engineering. He is married and the father of a son.

Following his graduation from the University of Utah he was employed by Hewlett Packard in Waltham, Massachusetts from 1967 to 1969. From 1969 to 1970 he was employed by Sylvania Electronics Systems Division, Needham, Massachusetts.

While at the University of Utah he was elected to Eta Kappa Nu, Tau Beta Pi and Phi Kappa Phi honor societies.